INTERFACIAL TENSION IN
LIGHT HYDROCARBON
BINARY SYSTEMS

By

LARRY DEAN SWALES

Bachelor of Science

Oklahoma State University

Stillwater, Oklahoma

1971

Submitted to the Faculty of the Graduate College
of the Oklahoma State University
in partial fulfillment of the requirements
for the Degree of
MASTER OF SCIENCE
July, 1972

INTERFACIAL TENSION IN

LIGHT HYDROCARBON

BINARY SYSTEMS

Thesis Approved:

R. N. Maddox
Thesis Adviser

John B. West

D. Durham
Dean of the Graduate College

PREFACE

Experimental interfacial tension data have been obtained for systems of ethane in propane, propane in normal butane, and propane in isobutane. Data were obtained at temperatures as close to the critical temperature, as predicted from a modified Rackett equation, as possible. The experimental data were compared to the interfacial tension predicted by the Ferguson equation for pure components and the Weinaug and Katz correlation for binary mixtures.

I wish to express my thanks to Dr. R. N. Maddox for his guidance as my thesis adviser. I would also like to thank Mr. M. B. Miller for his advice in handling the experimental apparatus.

I express my gratitude to the National Science Foundation for the financial support which enabled me to successfully complete my degree requirements.

Very special thanks go to my wife, Rosalyn, for her patience and encouragement during my graduate work.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF SYMBOLS

Major Symbols

<u>English Letters</u>

b	-radius of curvature of drop at origin
d_c	-capillary diameter, cm.
d_e	-drop equatorial diameter, cm.
d_s	-selected plane diameter, cm.
g	-acceleration of gravity, cm./sec.^{2}
H	-shape dependent parameter
M	-molecular weight
n	-exponent in Ferguson's equation
P	-pressure, p.s.i.a.
	pressure difference across a curved interface
[P]	-parachor
R and R'	-principal radii of curvature for curved surfaces
S	-liquid drop shape factor
T	-temperature, degrees R.
x	-mole fraction in liquid phase
y	-mole fraction in vapor phase

Greek Letters

β	-drop shape parameter
γ	-interfacial tension, dynes/cm.
γ_o	-Ferguson constant, dynes/cm.
δ	-uncertainty in measured quantity
ρ	-density, gm./cm.^{3}

Subscripts

c	-critical property
i	-component number
l	-liquid phase
r	-reduced property
v	-vapor phase

CHAPTER I

INTRODUCTION

Interfacial tension is a measure of the boundary energy existing between two phases. Interfacial tension is useful in characterizing some processes of heat transfer or mass transfer in multiphase systems. As there is a paucity of interfacial tension data available, this study was undertaken to fill in a few of the gaps in the available literature.

The goal of this study was to produce data on light hydrocarbon binaries near the critical region. Binaries of ethane in propane, propane in isobutane, and propane in normal butane were considered. The critical temperatures of these mixtures were between $100^{\circ}F$ and $310^{\circ}F$, temperatures common in industrial unit operations.

The experimental data were obtained using a pendant drop apparatus. In this method, liquid drops are suspended from a capillary tip into a vapor space. In this study, the vapor present was the equilibrium vapor of the liquid. A photograph is then taken of the drop. The interfacial tension is determined by measuring the equatorial diameter and a selected diameter of the drop from the photograph. This allows experimental measurements to be made without disturbing the drop during or prior to the acquisition of data. The photograph also provides a permanent record of the data.

CHAPTER II

LITERATURE SURVEY

In this work, the definitions of surface tension and interfacial tension of Andreas et al. (2) will be used. Andreas defines surface tension as the boundary tension between a liquid and a gas or vapor. The term interfacial tension applies when the liquid and the gas or vapor are in equilibrium.

The pendant drop method was used in this work to obtain interfacial tension. In this system, a drop of liquid is suspended from a capillary tip into an atmosphere of its equilibrium vapor. The composition of the liquid was fixed.

A mathematical description of the drop has been given by Deam (3) in accordance with earlier works. The description is based on the Laplace and Young Equation (1) for the pressure difference across the interface.

$$P = \gamma \left(1/R + 1/R' \right) \tag{1}$$

The expression for the surface tension, γ, derived from this equation is shown in Equation (2).

$$\gamma = \frac{g \left(\rho_l - \rho_v \right) d_e^{2}}{H} \tag{2}$$

Associated with this equation is a shape factor, S, defined in Equation (3).

$$S = d_s/d_e \tag{3}$$

The expression for the shape dependent parameter, 1/H, in Equation (2) is given in Equation (4).

$$1/H = - \frac{1}{\beta\, (\, d_e/b\,)^2} \tag{4}$$

As shown in Figure 1, d_e is the equatorial diameter of the drop, and d_s is the diameter of the drop at a selected plane a distance d_e from the vertex of the drop. The radius of curvature at the apex of the drop is denoted by b. The gravitational constant is g, and the phase densities are ρ_l and ρ_v. β is a parameter defined in Equation (5).

$$\beta = - gb^2 \; \frac{(\rho_l - \rho_v)}{\gamma} \tag{5}$$

Both b and β are difficult to measure precisely and quickly from a photograph of the drop, hence the shape factor (S) and the shape dependent parameter (1/H) are employed to describe the drop shape. Numerical tabulations of S as a function of 1/H have been prepared by Stauffer (15) for values of S from 0.30 to 0.66. Values of S from 0.67 to 1.00 as a function of 1/H have been determined by Fordham (7). Together, these tables cover the range of drop shapes normally encountered.

The procedure for determining the interfacial tension of a drop was to obtain a photograph of the drop, measure the selected and

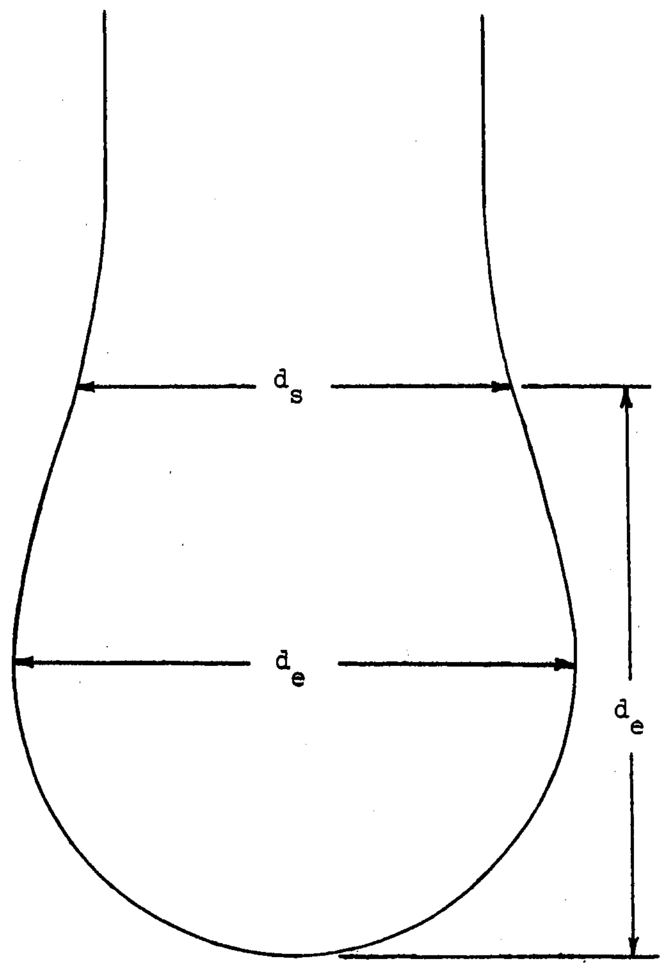

Figure 1. Pendant Drop Profile

equatorial diameters of the drop from the photographic negative, and then calculate the shape factor, S. Then the numerical tabulations of S as a function of 1/H were used to find 1/H. Finally, the interfacial tension was calculated from Equation (2).

Hough and Stegemeier used the pendant drop procedure to determine the interfacial tension of propane (8) and normal butane (9) near the critical temperature. The data obtained by these workers were compared to similar data obtained in this work. The data of Rossini, et al. (14), for isobutane were compared to the data obtained in this work.

As indicated by both Deam (3) and Niederhauser and Bartell (12), the pendant drop method is an absolute procedure; that is, it does not require calibration with a substance of known interfacial tension. A major advantage of the method is that, since a photograph of the drop is taken and the necessary measurements made from the photograph, no disturbance of the drop is necessary during or prior to the collection of data. The major drawback is the sensitivity of the clarity of the photographs to the alignment of the optical system. Any misalignment causes a photograph with blurred edges, thus introducing uncertainty into the drop measurements not due to the measuring instrument itself.

Predictive Correlations

For pure components, the correlation presented by van der Waals (16) and later confirmed by Ferguson (6) was adopted to predict the interfacial tension and to compare the predicted interfacial tension with experimentally obtained values. Ferguson's equation is given in Equation (6).

$$\gamma = \gamma_o \; (1 - T_r)^n \tag{6}$$

The correlation of Weinaug and Katz (17) was chosen for comparison with the experimental data of mixtures because of its applicability at elevated pressures. The equation these workers developed is given in Equation (7).

$$\gamma^{1/4} = \frac{\rho_l}{M_l} \Sigma \; x_i \; [P_i] - \frac{\rho_v}{M_v} \Sigma \; y_i \; [P_i] \tag{7}$$

Values of the parachor given by these authors were used with this correlation.

CHAPTER III

EXPERIMENTAL APPARATUS

The pendant drop apparatus employed for this study is predominantly the same as that used by Miller (10). Miller described the apparatus as being composed of five subsystems. These subsystems were the cell and temperature control subsystem, the instrumentation subsystem, the sample introduction subsystem, the evacuation and sample discharge subsystem, and the optical subsystem.

The only modification of this apparatus for use in this study was made to the sample introduction subsystem. A micrometer valve was installed between the inlet stop valve and the cylinder as shown in Figure 2. Drop sizes much smaller than those encountered by Miller were expected for this work, as data were to be taken near the critical temperature. At the critical temperature, the interfacial tension is identically zero. The micrometer valve was included to provide more precise control of the drop size than was possible with the existing equipment.

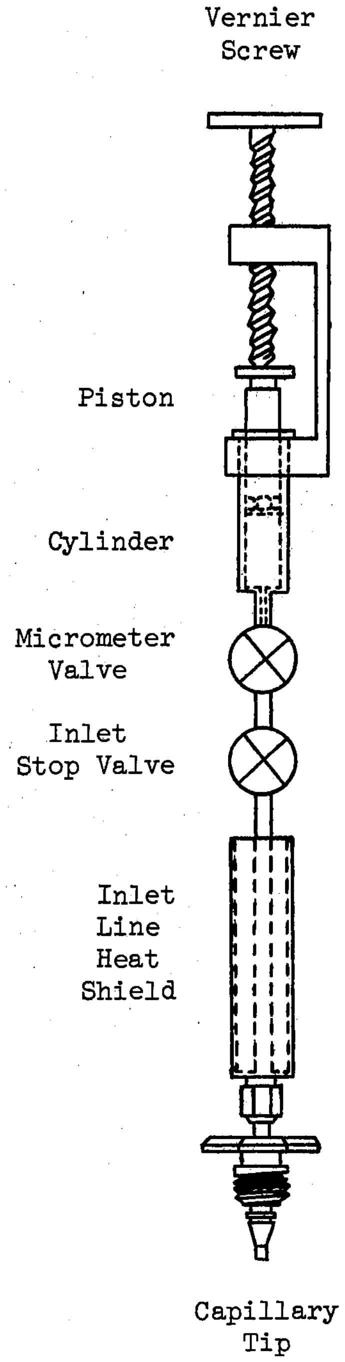

Figure 2. The Sample Introduction Subsystem

CHAPTER IV

EXPERIMENTAL PROCEDURE

An experimental run consisted of determining the interfacial tension of a mixture of known liquid composition for a number of different temperatures. The temperature range spanned from about 120°F to as near the critical temperature as possible. Normally, data were taken to within 15°F of the critical temperature.

The systems considered were propane in ethane, propane in isobutane, and propane in normal butane. The propane in ethane mixtures studied were thirty-four, seventy-four, and one hundred per cent propane, the propane in isobutane mixtures were zero, twenty-nine, seventy, and one hundred per cent propane, and the propane in normal butane mixtures were zero, seventy-three, and one hundred per cent propane. The source and purity of the chemicals used to prepare the mixtures were:

Component	Quality	Purity	Source
ethane	pure grade	99 mole % minimum	Phillips Petroleum Company
propane	instrument grade	99.5 mole % minimum	Phillips Petroleum Company
isobutane	instrument grade	99.5 mole % minimum	Phillips Petroleum Company
normal butane	instrument grade	99.5 mole % minimum	Phillips Petroleum Company

Before the start of each experimental run, the cell was cleaned. As the first step in cleaning the cell, it was evacuated to less than one inch of mercury absolute. Then, the cell was flushed with the heavier component of the system to be run. The final step in the cleaning procedure was to evacuate the cell again to a pressure of less than one inch of mercury.

After the cleaning procedure was completed, the cell was placed into an alcohol cooler in which the cell was cooled to approximately $-30^{\circ}F$. Then the heavier component was introduced into the liquid reservoir through the feed line and allowed to condense until liquid could be seen at the bottom of the viewport. Then the cell was immersed in the constant temperature bath and allowed to reach equilibrium at the lowest temperature for the run. As the liquid expanded on heating, enough was removed through the sample line to maintain the liquid level at the bottom of the viewport. This prevented damage to the O-ring seals which could occur if the liquid were permitted to completely fill the cell.

Thermal equilibrium was assumed when successive readings of both the liquid temperature and the vapor pressure taken at least thirty minutes apart were identical. The liquid temperature was monitored by an iron-constantan thermocouple in the liquid reservoir. A pressure transducer monitored the vapor pressure.

After thermal equilibrium was achieved, interfacial tension data were taken for the pure component. The needle valve and the micrometer valve in the feed line were opened and the piston was allowed to rise under the pressure inside the cell, thus sucking some of the vapor into the feed line. Since not all of the feed line was surrounded by the temperature bath, its temperature was slightly lower than that of the cell and the vapor condensed in the feed line. As soon as the vapor had sufficient time to condense, the piston was forced down into the cylinder with the vernier screw. This forced a drop of liquid to emerge from the tip of the capillary.

The extension of the drop from the capillary tip is an important element of the drop shape. The minimum extension for a useful drop, as indicated by Niederhauser and Bartell (12), is a drop length equal to its equatorial diameter. In this case the selected plane and the capillary tip are coincident. The maximum size drop is the largest drop that will remain on the capillary tip. Miller (10) describes a drop functioning like a lens in which light incident on one side is concentrated into two distinct regions. This indicates a drop larger than the minimum. This criterion was applied to drops used in this work.

Often during a run, it was necessary to change the capillary tip. This occurred when the drops became smaller than the capillary diameter, making the drop highly unstable and difficult to control. It also became necessary when the drops were so large as to be nearly spherical. These drops, according to Stauffer (15), have the highest inherent inaccuracy. Spherical drops occur when a capillary of too small diameter is used.

At temperatures where the interfacial tension was higher than three or four dynes per centimeter, the vernier screw gave adequate control over the drop size. However, at smaller values of interfacial tension, even very small adjustments of the vernier screw caused a cascade of drops instead of a single discrete drop. In this event, the micrometer valve just below the piston was utilized for drop control. The change in the total volume of the feed line as this valve closed was small enough to prevent forcing a cascade of drops out of the capillary. Once a drop was forced out, the valve could be opened or closed precisely enough for good drop control.

Once the drop has been formed and its extension adjusted, a photograph of the drop was taken. A number of photographs were taken at each temperature point. These photographs were then projected on the Vanguard CD-11 motion analyzer. The equatorial, capillary, and selected plane diameters were measured for each drop.

After data for the pure heavy component were taken, the cell was cooled to the lowest temperature for the first binary run and allowed to reach thermal equilibrium. The light component was then introduced through the sample line until the vapor pressure for the binary with the smallest amount of light component was reached. The N.G.P.A. K and H value program (5) was used to estimate this pressure. After allowing several hours for the system to reach equilibrium, a sample of the liquid was withdrawn through the sample line into a sample bomb. First, sufficient vapor was bled so that all vapor present in the line would be removed. Then the liquid was allowed to vaporize completely and discharge into the sample bomb. The bomb was filled to a pressure of about 35 psig. The composition was then checked by chromatographic analysis.

After the desired composition was reached, interfacial tension data were taken in the same manner as for the pure component. The composition was rechecked after each capillary change and at the end of each run to assure that no composition change had occurred during the run.

CHAPTER V

EXPERIMENTAL RESULTS

Experimental data were obtained for ethane in propane, propane in isobutane, and propane in normal butane. Data were taken at a number of compositions for each system. At each composition, data were obtained over a temperature range from 125°F to as near the critical temperature as possible. Since equilibrium was attained before any data were taken, the system pressure was the saturation pressure of the mixture at the system temperature.

To obtain the interfacial tension from the photographs of the liquid drops, the equatorial and selected diameters of each drop were first measured from the photographic negative. The shape dependent parameter of Equation (2), (d_e^2/H), was then calculated from these diameters. The liquid density was predicted from a modified Rackett equation (13) programmed for digital computer by Deam, Kellizy, and Maddox (4). The Redlich-Kwong equation of state as formulated in the N.G.P.A. K and H program (5) was used to predict the vapor density. The values of d_e^2/H, the liquid density, and the vapor density were then used in Equation (2) to calculate the interfacial tension.

The results of three compositions of ethane in propane are presented in Tables X - XII of Appendix B. Table I gives the arithmetic mean values of interfacial tension for these mixtures at

TABLE I

ARITHMETIC MEAN INTERFACIAL TENSIONS FOR THE ETHANE AND PROPANE BINARY SYSTEMS

Composition Mole % Ethane	Mean Temp. Degrees F.	Mean γ Dynes/cm.
0	120.6	4.05
	158.8	2.05
	178.7	0.91
	189.8	0.52
26	120.2	2.58
	140.4	1.60
	145.1	1.68
	149.6	1.38
66	99.8	1.30
	109.6	0.75
	114.7	0.67
	120.0	0.46
	122.1	0.29

their arithmetic mean temperature. These values of interfacial tension are plotted at constant composition in Figure 3 as a function of temperature.

Tables XIII through XV of Appendix B give the results of three compositions of propane in normal butane. The arithmetic mean values of interfacial tension at arithmetic mean temperature points are given in Table II. Figure 4 is a plot of these values of interfacial tension at constant composition as a function of temperature. Figure 5 is a cross plot from Figure 4 showing interfacial tension as a function of composition for lines of constant temperature.

Tables XVI through XVIII of Appendix B show the results of three compositions of propane in isobutane. Table III gives the arithmetic mean values of interfacial tension at arithmetic mean temperature points for these mixtures. This data is shown in Figure 6 as a plot of interfacial tension as a function of temperature at constant composition. Figure 7 is a cross plot from Figure 6 showing interfacial tension as a function of composition for several isotherms.

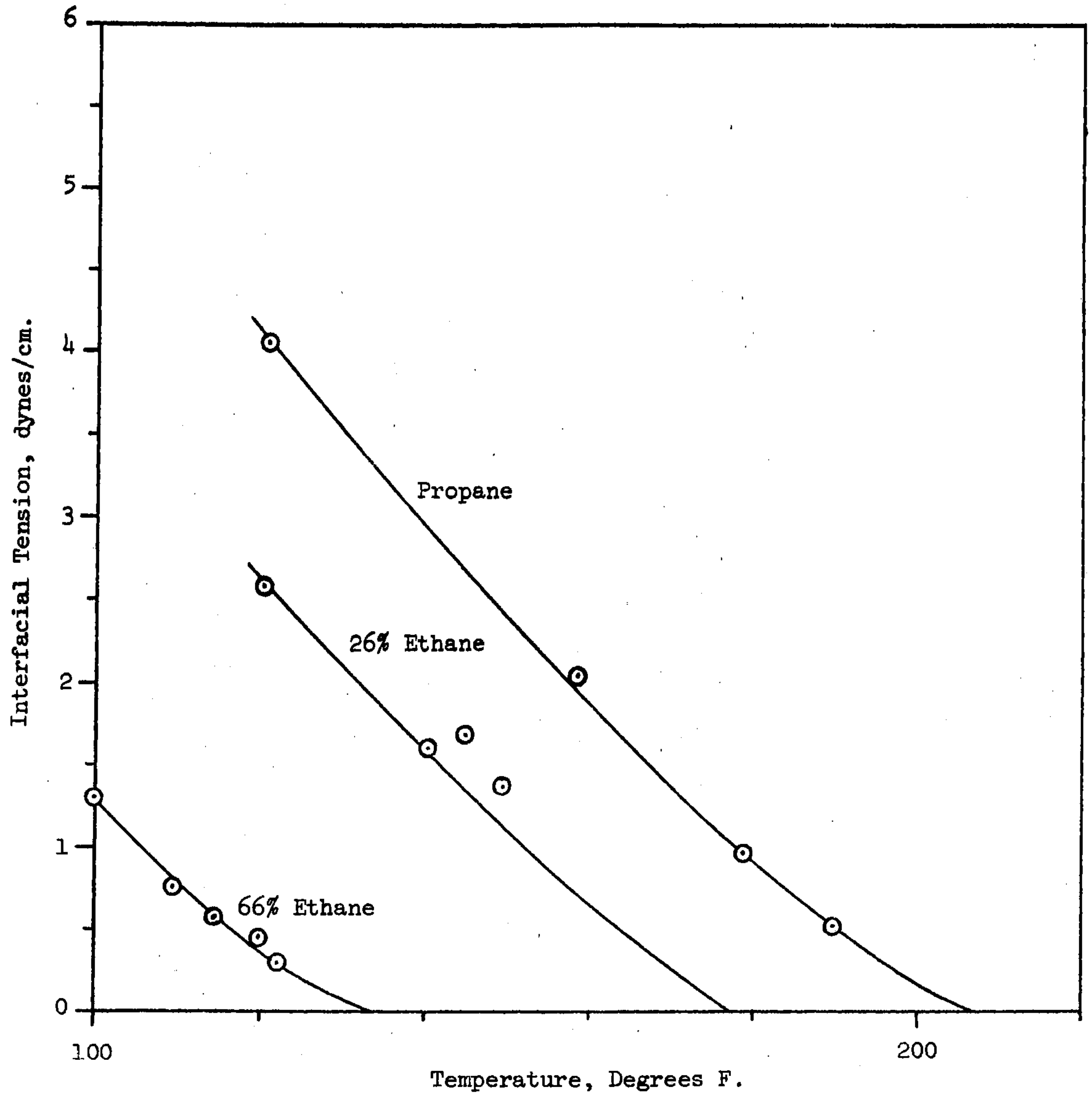

Figure 3. The Interfacial Tension for Mixtures of Ethane and Propane, as a Function of Temperature

TABLE II

ARITHMETIC MEAN INTERFACIAL TENSIONS FOR
THE PROPANE AND NORMAL BUTANE
BINARY SYSTEMS

Composition Mole % Propane	Mean Temp. Degrees F.	Mean γ Dynes/cm.
0	125.6	9.03
	150.3	7.61
	200.6	4.75
	224.6	3.45
	249.4	2.05
	276.0	0.86
	285.0	0.55
30	124.3	8.54
	150.2	6.76
	199.1	3.71
	224.2	2.22
	248.4	0.71
	260.8	0.25
73	150.4	4.41
	175.5	2.56
	196.7	1.79
	209.1	1.01
	224.8	0.34
	229.6	0.15

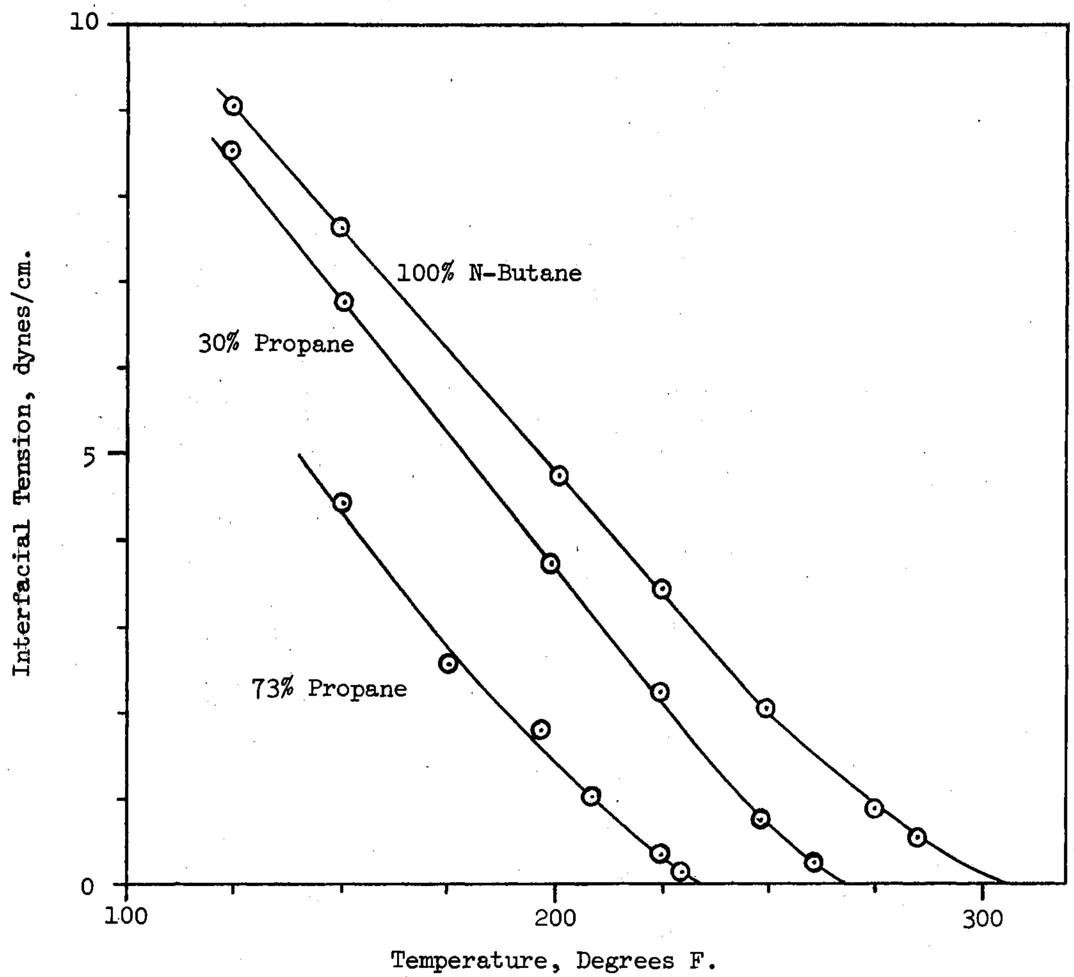

Figure 4. The Interfacial Tension for Mixtures of Propane and Normal Butane, as a Function of Temperature

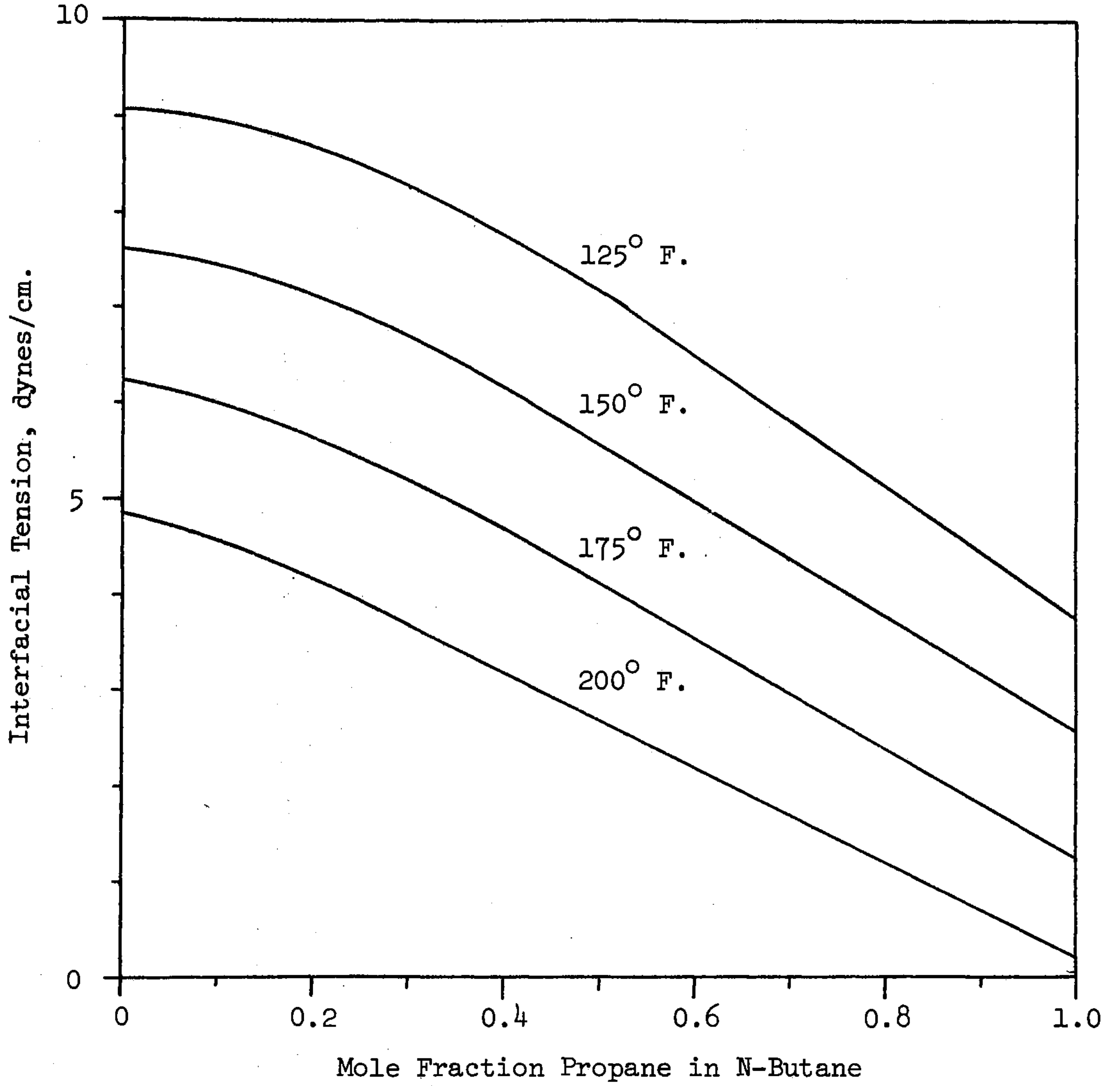

Figure 5. The Interfacial Tension for Mixtures of Propane and Normal Butane, as a Function of Composition

TABLE III

ARITHMETIC MEAN INTERFACIAL TENSIONS FOR
THE PROPANE AND ISOBUTANE
BINARY SYSTEMS

Composition Mole % Propane	Mean Temp. Degrees F.	Mean γ Dynes/cm.
0	125.2	6.74
	150.1	5.68
	175.1	4.28
	200.2	2.95
	224.9	1.64
	247.5	0.72
	262.6	0.25
29	124.2	6.14
	149.8	4.94
	173.3	3.55
	199.8	2.13
	223.7	0.98
	236.6	0.49
	244.6	0.26
70	126.1	4.89
	150.5	3.44
	176.0	2.21
	200.6	0.95
	215.1	0.34
	219.1	0.20

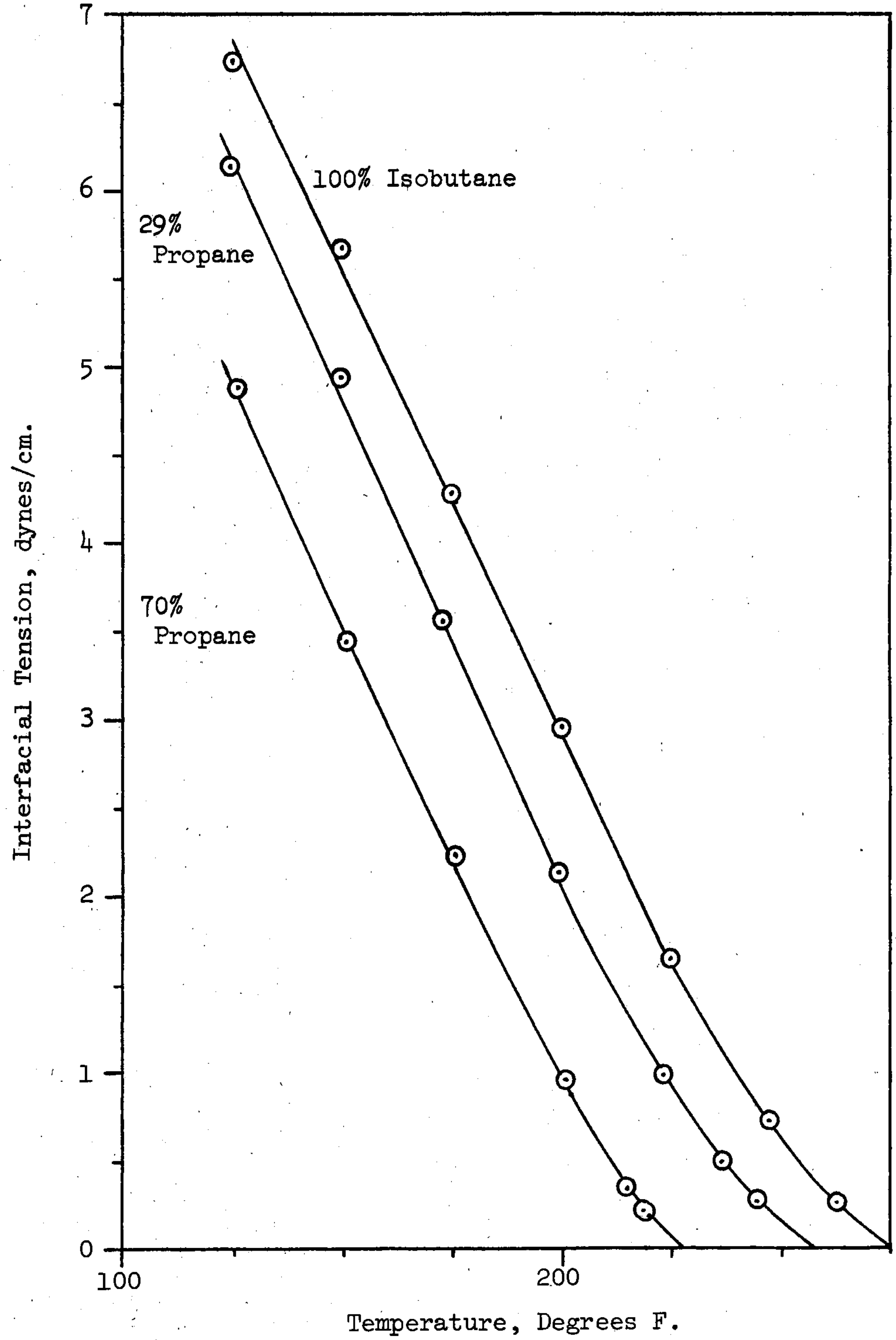

Figure 6. The Interfacial Tension for Mixtures of Propane and Isobutane, as a Function of Temperature

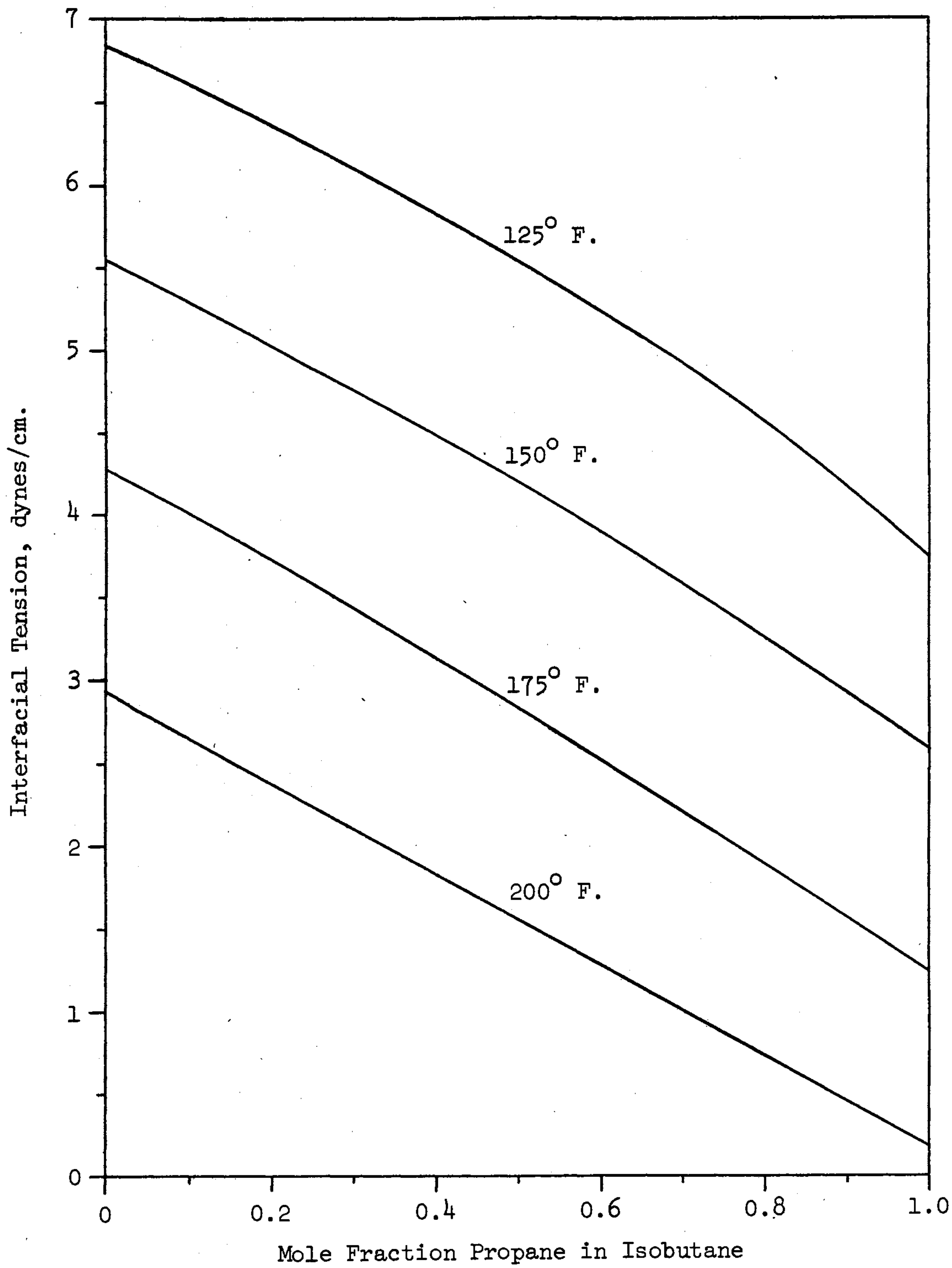

Figure 7. The Interfacial Tension for Mixtures of Propane and Isobutane, as a Function of Composition

CHAPTER VI

DISCUSSION OF RESULTS

The experimental data obtained in this work for pure propane and pure normal butane were compared with similar data available in the literature. The available literature for isobutane does not include data near the critical temperature, so the data of this work was compared with data at lower temperatures.

The experimental data for the pure components were also compared with the interfacial tension predicted by the correlation of Ferguson (6). Data for each of the mixtures were compared with the interfacial tension predicted by the correlation developed by Weinaug and Katz (17).

The Ferguson equation constants for propane and normal butane were evaluated from the data of Hough and Stegemeier (8)(9). The constants for isobutane were derived from the curves found in the 1966 N.G.P.S.A. data book (11). Parachors for each component were taken from the paper by Weinaug and Katz describing their correlation. The liquid densities needed for the Weinaug and Katz correlation were evaluated through the modified Rackett program (4). Molecular weights, vapor phase compositions, and vapor phase densities were obtained through the N.G.P.A. K and H program (5). Critical constants were taken from the 1966 N.G.P.S.A. data book.

The most probable error of the method by which the data were obtained is shown in Appendix C to be $\pm$ 0.19 dynes/cm. The two limiting factors of the precision were the precision of the measuring device used to measure the diameters of the drop and the accuracy of the density difference information used. The effect of these factors on the most probable error is the value given above.

Constant liquid composition throughout each experimental binary run was assured by chromatographic analysis of a liquid sample before the start of each run, after each capillary change, and at the end of the run. In all cases, no detectable change occurred during the run. The chromatographic analysis could detect a change of one mole per cent or larger.

Although Equation (2) was developed specifically for a static drop, a study comparing the interfacial tension calculated from photographs of drops in motion with the interfacial tension of static drops indicated that some motion can be tolerated. At least one photograph of a drop in motion was obtained for the thirty per cent propane and seventy per cent normal butane binary at 124.3°F., 150.2°F., 248.4°F., and 260.8°F. The mean interfacial tension at these temperatures ranged from 8.54 dynes/cm. to 0.25 dynes/cm. In each case, the interfacial tension calculated from the photograph of the moving drop fell within the range of interfacial tension values calculated from photographs of the static drops. Data were also obtained for nine drops of the seventy per cent isobutane and thirty per cent propane binary at 199.8°F. Four of these drops were static and the other five were moving to some degree when the photographs were taken. The mean interfacial tension of the four static drops was 2.12 dynes/cm. compared with a mean interfacial tension of 2.14 dynes/cm. for the five drops in motion. The range of interfacial tension values for the two groups of drops was similarly comparable. The four static drops showed a range of 2.03 to 2.19 dynes/cm., while the range of the five moving drops was 2.07 to 2.19 dynes/cm.

Each of the drops in motion met two criteria. The time elapsed from the moment the drop began to emerge from the capillary tip until it fell from the tip of the capillary was at least one second. Drops falling faster than this often produced blurred photographs or tended to coalesce into a continuous stream of fluid. Drops moving this quickly also tended to vibrate from side to side. Photographs of drops moving from side to side were blurred on either side, thus prohibiting the measurement of the drop diameters, or they were distinctly asymmetrical. The drop shape of asymmetrical drops cannot be characterized by the drop shape parameter, 1/H. The minimum time of one second applies to drops of 2 dynes/cm. interfacial tension or smaller. Larger drops need proportionately longer formation times to be useful. Each of the drops also met the requirement for extension from the capillary tip explained previously. The necessity of photographing the drop when it is properly extended from the capillary tip is a further reason to use only those drops falling more than one second after they begin to form.

Propane Experimental Results

The arithmetic mean data points for propane, as shown in Table I, are compared graphically with the smoothed data of Hough and Stegemeier (8) in Figure 8. The experimental data of this work agree quite well with the data obtained by Hough and Stegemeier. The experimental data for propane showed an average absolute deviation

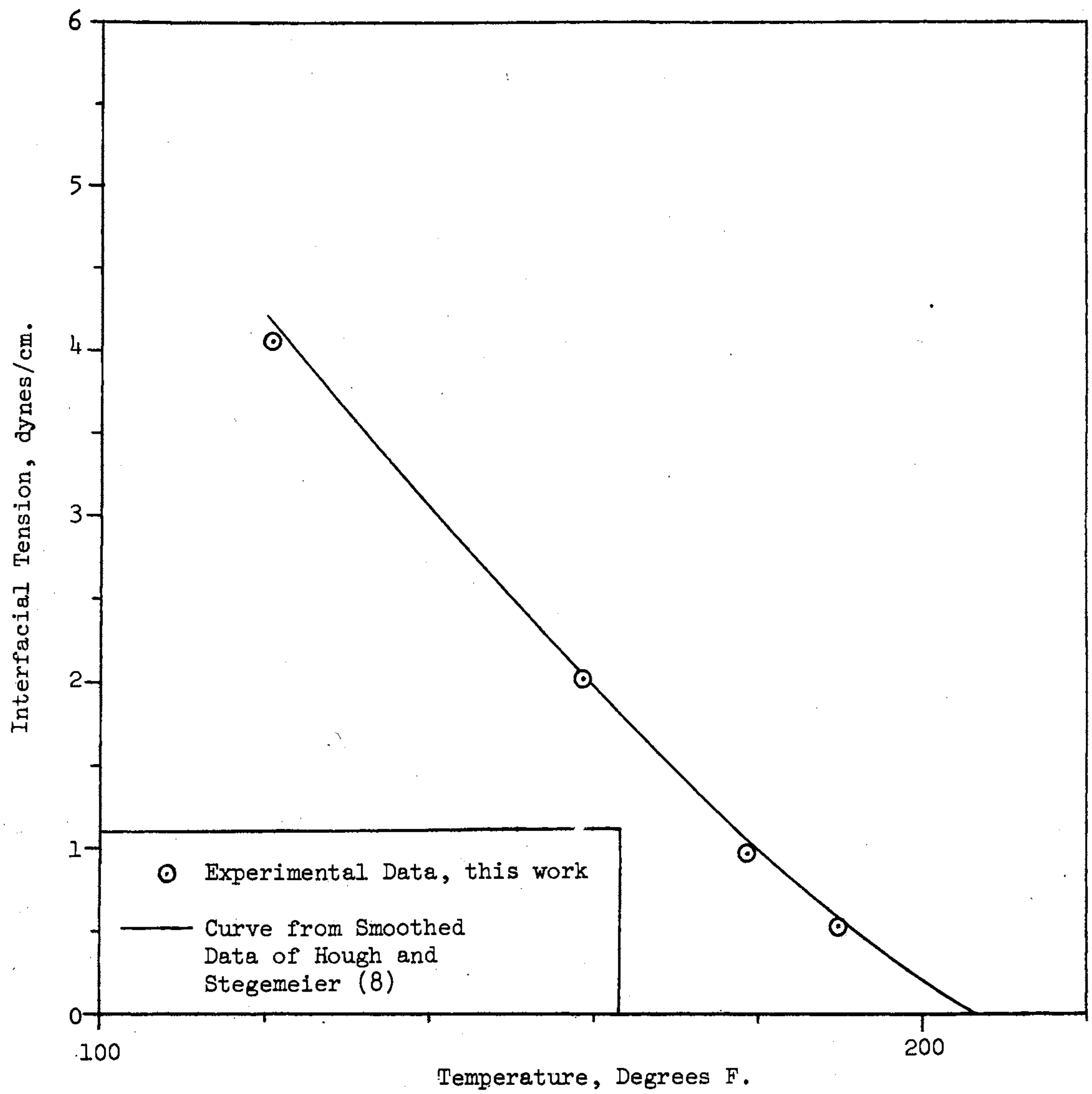

Figure 8. Comparison of Experimental Interfacial Tension for Pure Propane to Data from Previous Works

of 0.03 dynes/cm. from the mean data points. The mean data were compared with the interfacial tension predicted by the method of Ferguson. The result of this comparison is shown in Table IV. The average absolute deviation of the predicted values from the experimental values was 10.22%.

Normal Butane Experimental Results

The result of a comparison of the experimental data for normal butane with the data of Hough and Stegemeier (9) is shown graphically in Figure 9. The experimental data points were the arithmetic mean values of Table II. Again the experimental data of this work show very good agreement with the data of Hough and Stegemeier. The experimental data for normal butane had an average absolute deviation of 0.10 dynes/cm. from the arithmetic mean data. In Table V the experimental data are compared with the interfacial tension predicted by Ferguson's equation. The predicted values showed an average absolute deviation of 6.16% from the mean data points.

Isobutane Experimental Results

Figure 10 shows the experimental data points of Table III in conjunction with the data of Rossini, et al. (14), which was taken at much lower temperatures. The graph indicates the two sets of data are reasonably compatible, although the data of Rossini were taken in air rather than in the equilibrium vapor. The average absolute deviation of the experimental data from the arithmetic mean data was 0.06 dynes/cm. The interfacial tension values predicted from Ferguson's equation are compared in Table VI with the arithmetic mean data points.

TABLE IV

PREDICTED INTERFACIAL TENSION
OF PROPANE

Temp. Degrees F.	Interfacial Tension in dynes/cm. Mean Data	Ferguson Equation
120.6	4.05	4.26
158.8	2.05	2.10
178.7	0.91	1.09
189.8	0.52	0.59

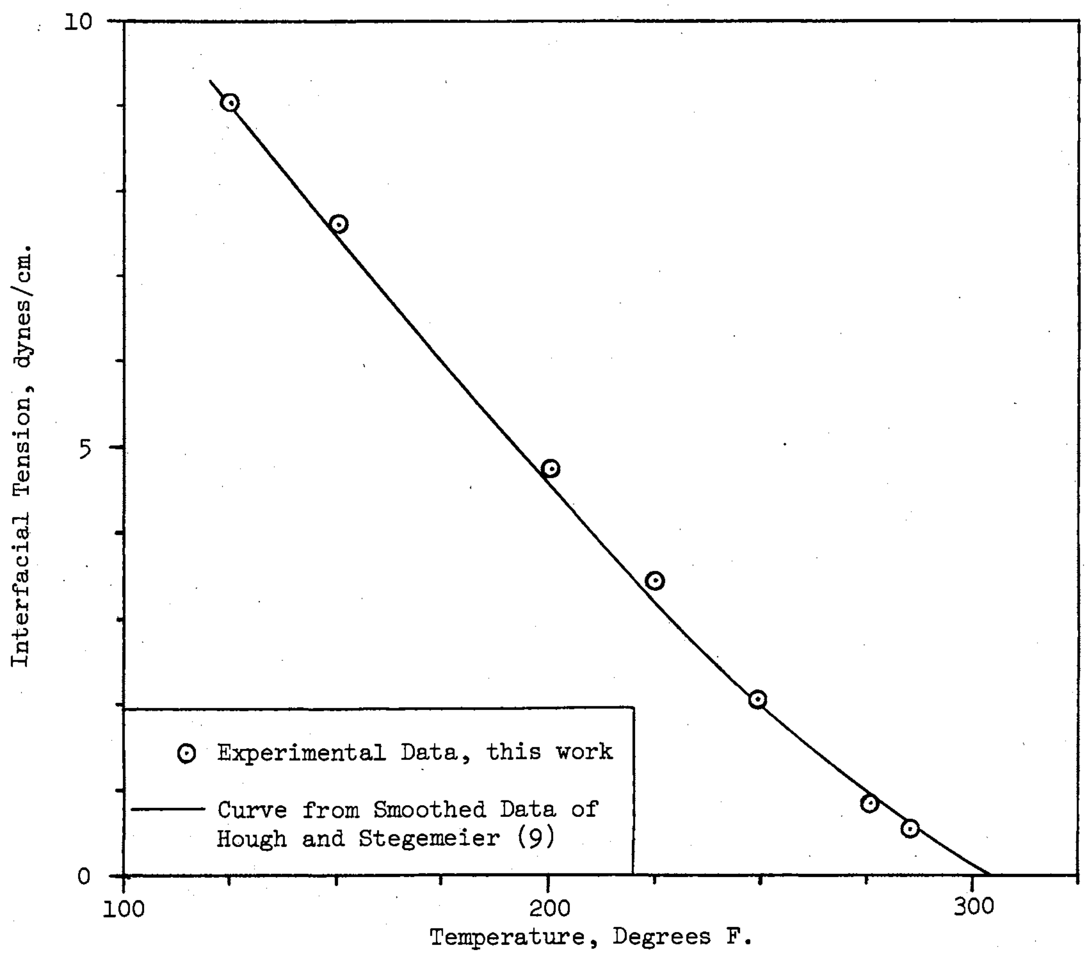

Figure 9. Comparison of Experimental Interfacial Tension for Pure Normal Butane to Data from Previous Works

TABLE V

PREDICTED INTERFACIAL TENSION
OF NORMAL BUTANE

Temp. Degrees F.	Interfacial Tension in dynes/cm. Mean Data	Interfacial Tension in dynes/cm. Ferguson Equation
125.6	9.03	8.98
150.3	7.61	7.50
200.6	4.75	4.65
224.6	3.45	3.39
249.4	2.05	2.17
276.0	0.86	0.99
285.0	0.55	0.64

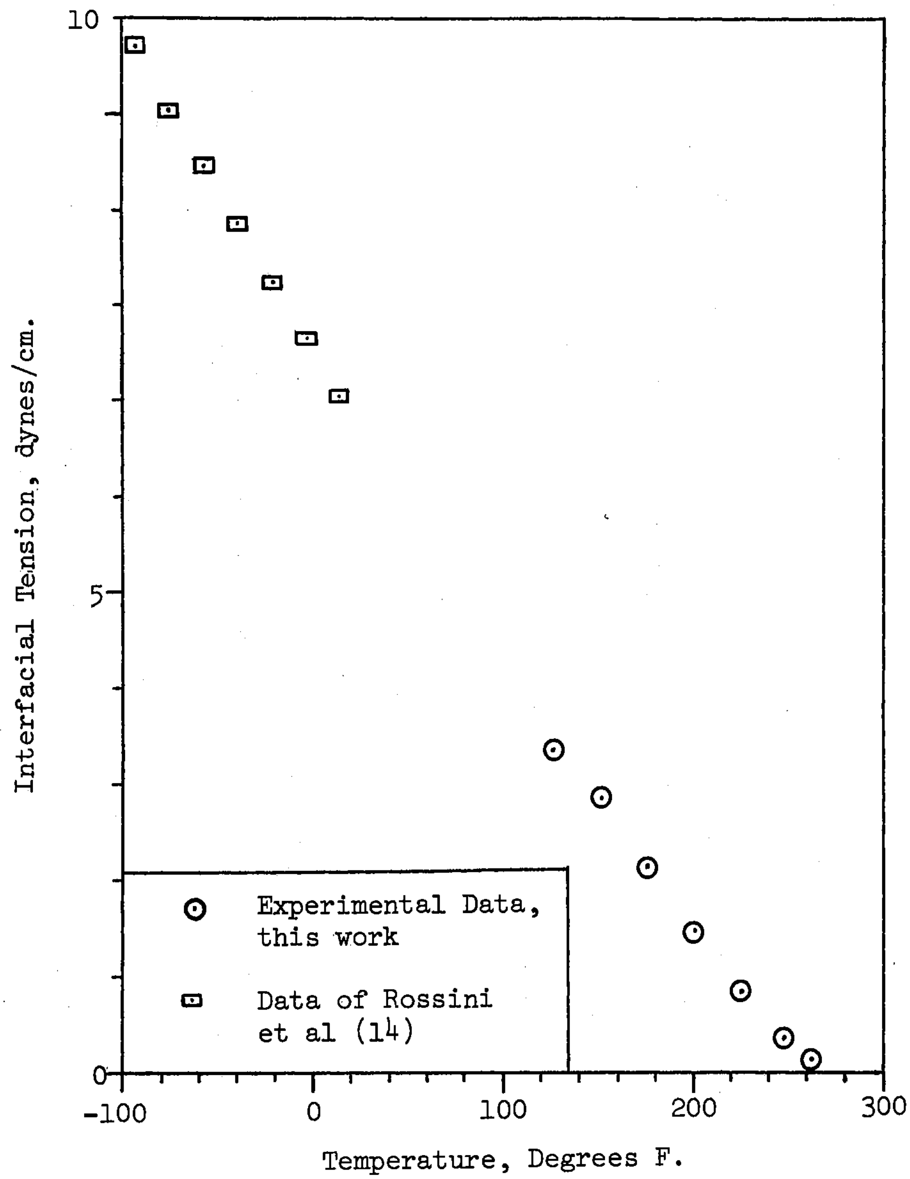

Figure 10. Comparison of Experimental Interfacial Tension for Pure Isobutane to Data from Previous Works

TABLE VI

PREDICTED INTERFACIAL TENSION
OF ISOBUTANE

Temp. Degrees F.	Interfacial Tension in dynes/cm.	
	Mean Data	Ferguson Equation
125.2	6.74	6.90
150.1	5.68	5.45
175.1	4.28	4.08
200.2	2.95	2.80
224.9	1.64	1.66
247.5	0.72	0.76
262.6	0.25	0.27

The predicted values exhibited an average absolute deviation of 4.29% from the mean experimental data.

Mixtures of Ethane and Propane

The arithmetic mean data of mixtures of ethane and propane were presented in Table I. The average absolute deviation of the data for the twenty-six per cent ethane binary was 0.11 dynes/cm. The average absolute deviation for the sixty-six per cent ethane binary was 0.07 dynes/cm. Since the interfacial tension reaches zero at the critical temperature, the curves in Figure 2 were extended to the critical temperature. The modified Rackett program (4) was used to estimate the critical temperatures of these mixtures. The critical temperatures predicted were 177°F. for twenty-six per cent ethane and 133°F. for sixty-six per cent ethane. The data points at 141.5°F. and 149.6°F. for the twenty-six per cent ethane binary were judged to be too high by 0.29 and 0.22 dynes/cm., respectively. This error was most likely due to misalignment of the optical system which resulted in rather blurred photographs. This defect was corrected before further data were taken.

The experimental data for these mixtures were compared with the interfacial tension predicted by the correlation of Weinaug and Katz. In Table VII, the result of this comparison is presented. The average absolute deviation of the predicted values from the experimental values was 22.66% for the twenty-six per cent ethane mixture and 17.03% for the sixty-six per cent ethane binary. In every instance, the predicted values were lower than the experimental values.

TABLE VII

INTERFACIAL TENSION OF MIXTURES OF ETHANE AND PROPANE

Mole % Ethane	Temp. Degrees F.	Interfacial Tension in dynes/cm. Mean Data	Interfacial Tension in dynes/cm. Weinaug and Katz Equation
26	120.2	2.58	2.38
	140.4	1.60	1.34
	145.1	1.68	1.12
	149.6	1.38	0.92
66	99.8	1.30	1.12
	109.6	0.75	0.70
	114.7	0.67	0.51
	120.0	0.46	0.32
	122.1	0.29	0.26

Mixtures of Propane and Normal Butane

Table II showed the arithmetic mean data for mixtures of propane in normal butane containing thirty and seventy-three per cent propane. The average absolute deviation of the data was 0.08 dynes/cm. for the thirty per cent propane mixture and 0.06 dynes/cm. for the binary with seventy-three per cent propane. The curves drawn through the experimental data in Figure 4 were extended to zero at the critical temperatures of the mixtures. The critical temperatures were 268°F. for the thirty per cent propane mixture and 234°F. for the seventy-three per cent propane binary as predicted by the modified Rackett program.

The curves of interfacial tension as a function of composition for lines of constant temperature in Figure 5 were derived from Figure 4 and the propane curve of Figure 3. These curves showed a slightly smaller rate of change of interfacial tension with composition near the component of higher interfacial tension, the normal butane. However, the curves are nearly linear and become increasingly so as the temperature increases. This nearly ideal behavior is not unexpected for two components related as closely as are propane and normal butane.

The arithmetic mean data points of Table II were compared with the interfacial tension predicted from the Weinaug and Katz equation. The result of this comparison is presented in Table VIII. There was an average absolute deviation of 22.12% from the data for the thirty per cent propane binary and a deviation of 24.80% from the experimental data for the seventy-three per cent propane mixture.

TABLE VIII

INTERFACIAL TENSION OF MIXTURES OF PROPANE AND NORMAL BUTANE

		Interfacial Tension in dynes/cm.	
Mole % Propane	Temp. Degrees F.	Mean Data	Weinaug and Katz Equation
30	124.3	8.54	7.33
	150.2	6.76	5.79
	199.1	3.71	3.09
	224.2	2.22	1.86
	248.4	0.71	0.83
	260.8	0.25	0.40
73	150.4	4.41	3.67
	175.5	2.56	2.30
	196.7	1.79	1.28
	209.1	1.01	0.76
	224.8	0.34	0.22
	229.6	0.15	0.10

TABLE IX

INTERFACIAL TENSION OF MIXTURES OF PROPANE AND ISOBUTANE

		Interfacial Tension in dynes/cm.	
Mole % Propane	Temp. Degrees F.	Mean Data	Weinaug and Katz Equation
29	124.2	6.14	4.69
	149.8	4.94	3.56
	173.3	3.55	2.57
	199.8	2.13	1.54
	223.7	0.98	0.72
	236.6	0.49	0.35
	244.6	0.26	0.15
70	126.1	4.89	4.15
	150.5	3.44	2.90
	176.0	2.21	1.70
	200.6	0.95	0.71
	215.1	0.34	0.23
	219.1	0.20	0.12

from the data for the seventy per cent propane mixture. The predicted values of interfacial tension were consistently lower than the experimental values.

CHAPTER VII

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

The purpose of this study was to investigate the behavior of the interfacial tension of binary mixtures as the critical temperature was approached. Experimental data were obtained for mixtures of ethane in propane, propane in normal butane, and propane in isobutane. Data were also obtained for the pure substances propane, normal butane, and isobutane. The curves of interfacial tension as a function of temperature exhibited an increasing rate of change with temperature as the critical temperature was approached. The experimental data obtained for normal butane and propane were compared to corresponding data in the literature and were found to agree well with that data.

Experimental data were compared with predicted values of interfacial tension from an appropriate correlation. Ferguson's equation, used with pure components, agreed well with the experimental data. The average absolute deviation of values of interfacial tension predicted from the correlation of Ferguson from the mean data ranged from 4.3% to 10.2%. The correlation of Weinaug and Katz was used for the mixtures. Values of interfacial tension predicted from the Weinaug and Katz equation were lower than the values that were obtained experimentally. The average absolute deviation of interfacial tension values predicted by the correlation from the mean data points ranged from 17.0% to 29.2%.

Recommendations

The single major factor in the speed with which data could be taken and the reliability of this data was the quality of drop control that could be derived from the apparatus. The major defect of the drop control system of the apparatus used in this study was inadequate shielding of the feed system from thermal effects. Often, a drop was pulled back into the capillary or forced off the tip with a jet of liquid caused by thermal contraction or expansion in the feed line before a photograph of the drop could be taken.

Much of this could be eliminated by two modifications to the inlet line heat shield. One modification is to weld the heat shield to the top of the fitting connecting the inlet line to the vapor chamber. This would eliminate about four inches of exposed fittings now necessary to attach the heat shield to the feed line. The other change is to plug the presently open upper end of the heat shield, providing two ports in the plug to allow the flow of water or air through the space between the heat shield and the inlet line. Figure 11 shows these modifications. The combination of these two system adjustments should give greater control over drop formation.

It is also recommended that experimental density difference data be obtained for the binary systems considered in this study. This information, when used with the values of d_e^2/H in Appendix B, could increase the reliability of the interfacial tension of the binary mixtures, particularly near the critical temperature.

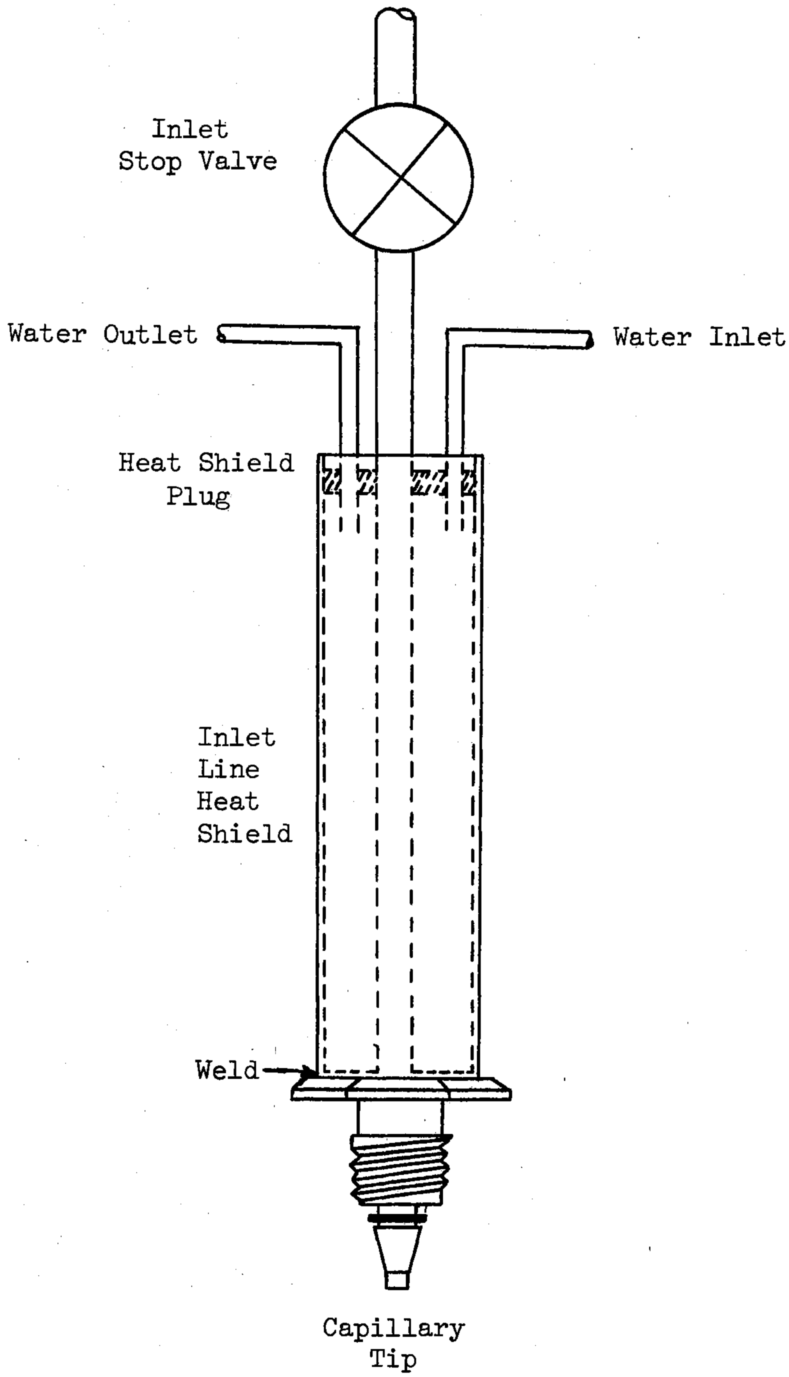

Figure 11. Recommended Modifications to the Sample Introduction Subsystem

A SELECTED BIBLIOGRAPHY

(1) Adamson, A. W. Physical Chemistry of Surfaces. New York: Interscience Publishers, Inc., 1960.

(2) Andreas, J. M., E. A. Hauser, and W. B. Tucker, "Boundary Tension by Pendant Drops." Journal of Physical Chemistry 43. 1001 (1938).

(3) Deam, J. R. "Interfacial Tension in Hydrocarbon Systems." (Unpub. Ph.D. thesis, Oklahoma State University, 1969).

(4) Deam, J. R., I. K. Kellizy, and R. N. Maddox. "Calculating Density of Saturated Hydrocarbon Mixtures." Proceedings of the Forty-Eighth Annual Convention. N.G.P.A., 48 (1969).

(5) Erbar, J. H. "K & H Computer Program, I. B. M. Series 360." N.G.P.A. (1966).

(6) Ferguson, A. "On A Relation Between Surface Tension and Density." Transactions of Farady Society 19, 407 (1923).

(7) Fordham, S. "On the Calculation of Surface Tension from Measurements of Pendant Drops." Proceedings of the Royal Society 194A (London). 1 (1948).

(8) Hough, E. W., and G. L. Stegemeier. "Surface Tension of Propane Near the Critical." Producers Monthly 26. number 6, 21 (1962).

(9) Hough, E. W., and G. L. Stegemeier. "Surface Tension of Normal Butane Near the Critical." Producers Monthly 26. number 6, 20 (1962).

(10) Miller, M. B. "Experimental Determination of the Interfacial Tension of Binary Systems." (Unpub. Masters thesis, Oklahoma State University, 1972).

(11) N. G. P. S. A. Engineering Data Book. Tulsa, Oklahoma, 1966.

(12) Niederhauser, D. O., and F. E. Bartell. "A Corrected Table for the Calculation of Boundary Tensions by the Pendant Drop Method." Report of Progress -- Fundamental Research on Occurrence and Recovery of Petroleum. A. P. I., Baltimore, Md., 114 (1950).

(13) Rackett, H. G. "Equations of State for Saturated Liquids." Journal of Chemical and Engineering Data 15. 514 (1970).

(14) Rossini, F. D., K. S. Pitzer, R. L. Arnett, R. M. Braum, and G. C. Pimentel. Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds. Pittsburgh, Pennsylvania: Carnegie Press, 1953.

(15) Stauffer, C. E. "The Measurement of Surface Tension by the Pendant Drop Technique." Journal of Physical Chemistry 69. 1933 (1965).

(16) van der Waals, J. D. Zeitschrift fur Physikalische Chemie 13. 617 (1894).

(17) Weinaug, C. F., and D. L. Katz. "Surface Tension of Methane - Propane Mixtures." Ind. and Eng. Chem. 35. 239 (1943).

APPENDIX A

INSTRUMENTATION CALIBRATION

CURVES

Instrument Calibrations

Calibration curves for the cell thermocouple and the pressure transducer used to monitor the system temperature and pressure, respectively, were prepared. The thermocouple was calibrated against three reference temperatures; the melting point of tin at 449.4°F., the boiling point of distilled water under an atmospheric pressure of 746 mm. Hg at 210.9°F., and the melting point of distilled water at 32°F. Figure 12 shows the thermocouple calibration curve so obtained. The pressure transducer was calibrated against a Budenberg dead weight guage tester, number 2167. The pressure transducer calibration curve is presented in Figure 13.

The chromatograph was also calibrated for each binary system studied. Standard samples were prepared first by choosing a total pressure to which the sample bomb was to be filled. The Redlich-Kwong equation of state was then used to determine the total number of moles in the sample bomb when filled to this pressure. This number multiplied by the mole fraction of one component, A, gave the number of moles of that component in the standard sample. The Redlich-Kwong equation was again used to determine the pressure to which the sample bomb needed to be filled with component A to give this number of moles. Then the sample bomb was filled to this pressure with component A. The other component was then introduced into the sample bomb until the pressure in the bomb reached the initially chosen value. Each standard was analyzed at least ten times on a gas chromatograph with a thermal conductivity detector. A ten foot by one-quarter inch column packed with Davison grade 08 silica gel was used to effect the

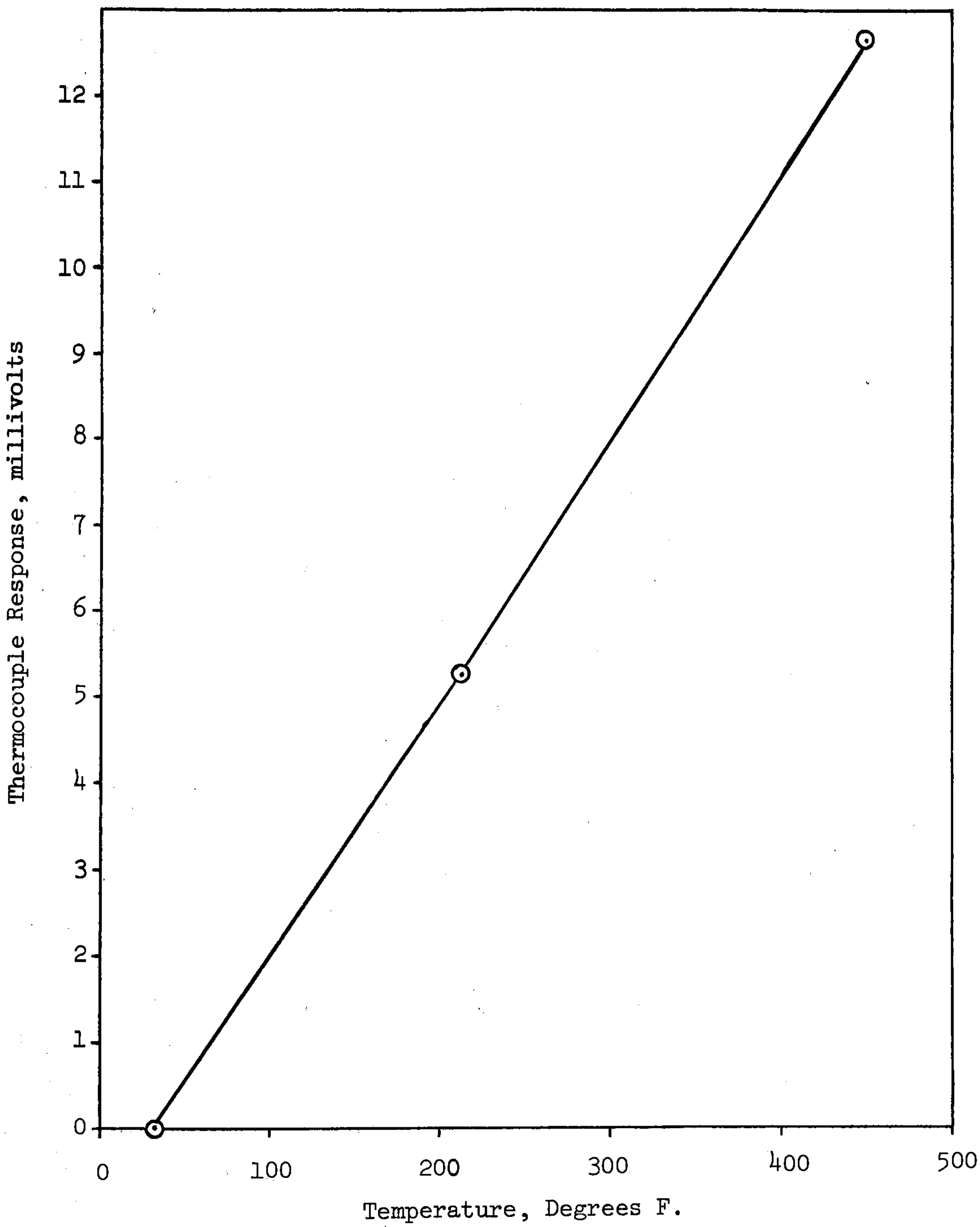

Figure 12. Thermocouple Calibration Curve

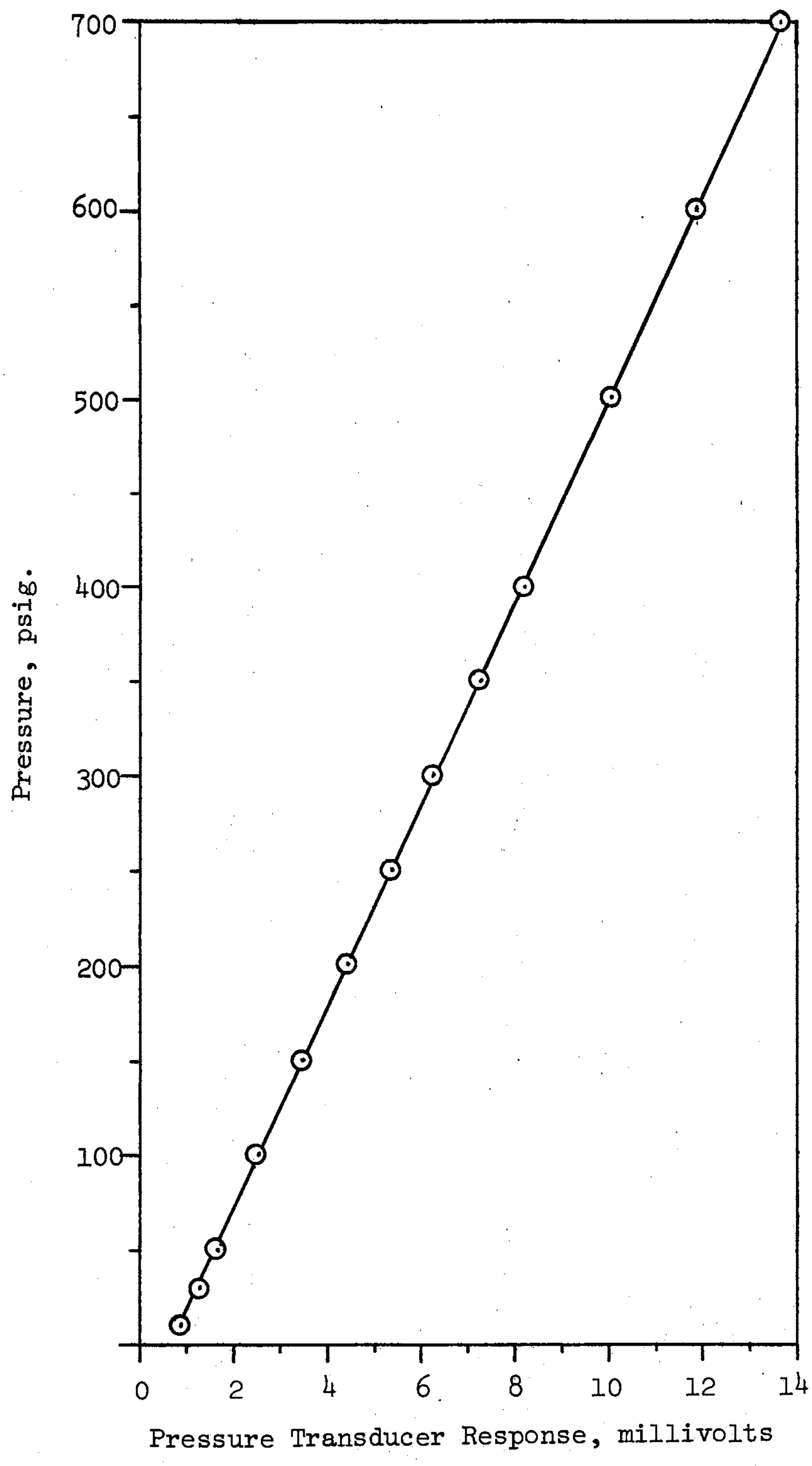

Figure 13. Pressure Transducer Calibration Curve

the separation. The area of each peak was measured by a Perkin-Elmer D2 integrator. After each analysis, the area of the peak of the light component was divided by the sum of the areas of the peaks for both components. The arithmetic mean of these ratios was taken for each standard sample and plotted as a function of the mole fraction of the light component in the standard. Figures 14, 15, and 16 are these plots for ethane in propane, propane in normal butane, and propane in isobutane, respectively.

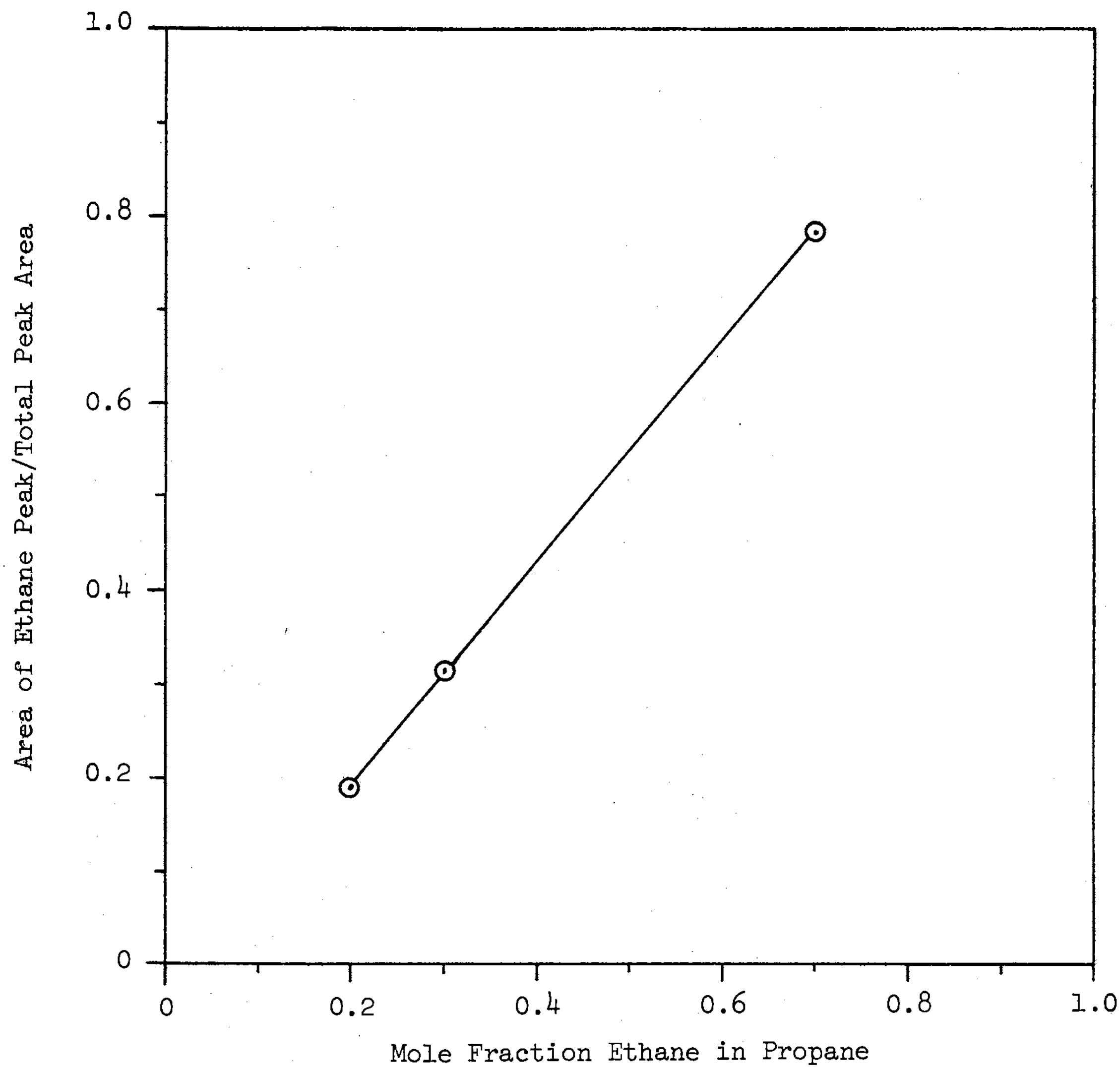

Figure 14. Chromatograph Calibration Curve for the Ethane and Propane Binary Systems

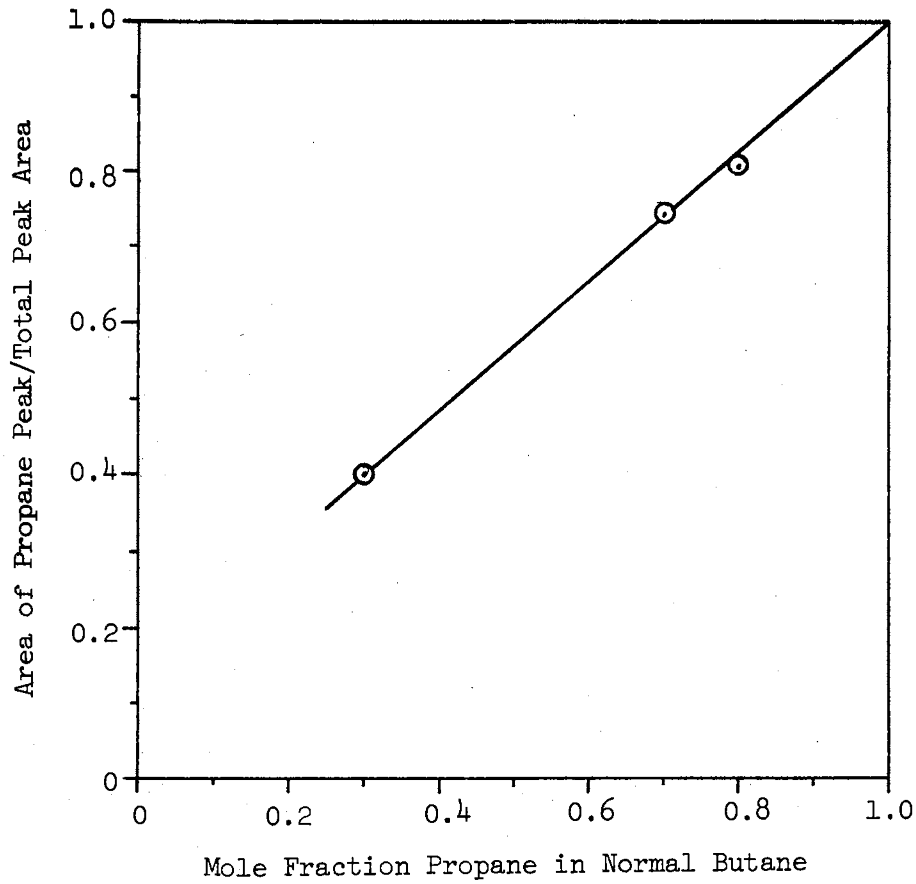

Figure 15. Chromatograph Calibration Curve for the Propane and Normal Butane Binary Systems

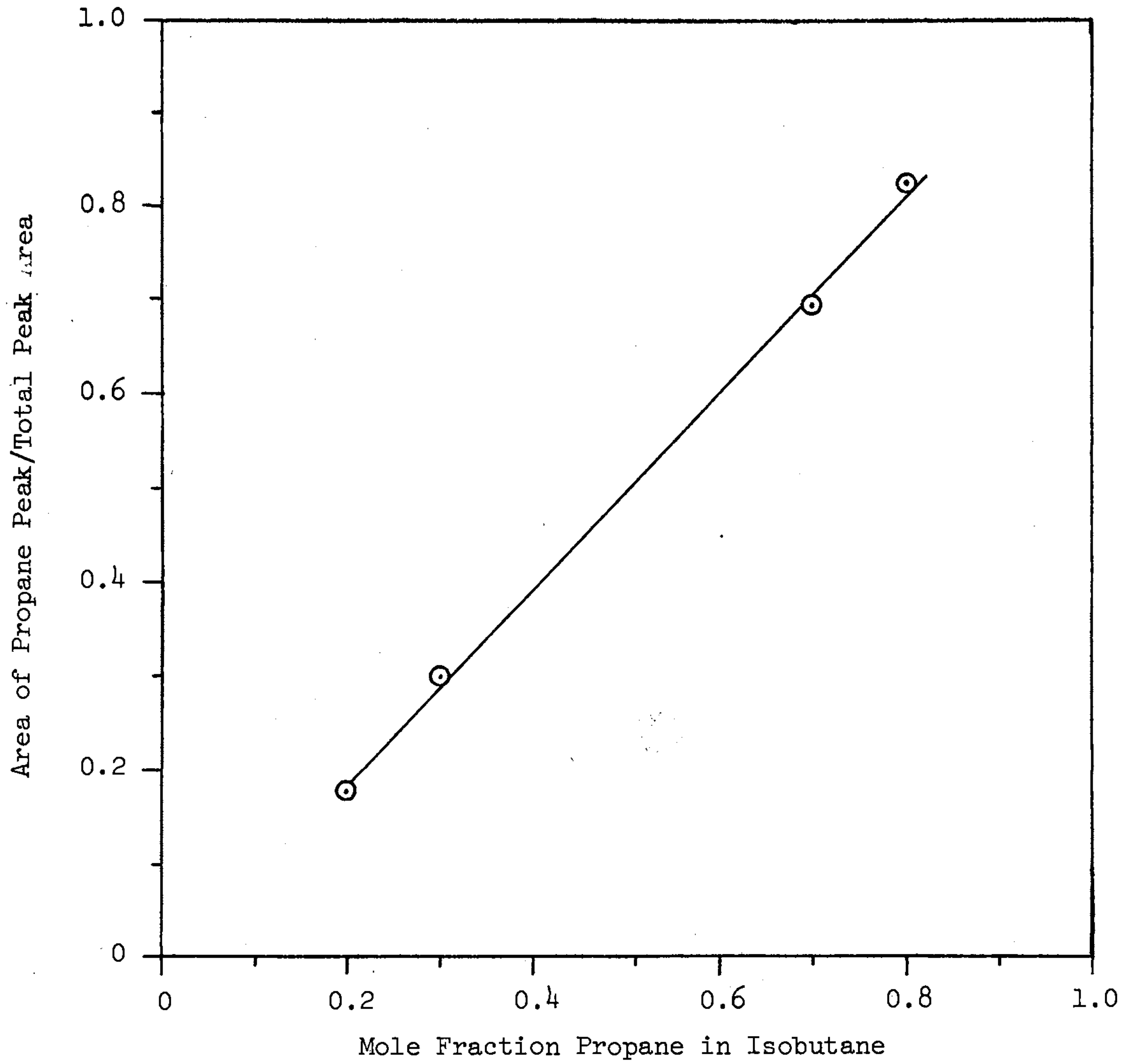

Figure 16. Chromatograph Calibration Curve for the Propane and Isobutane Binary Systems

APPENDIX B

EXPERIMENTAL DATA

TABLE X

EXPERIMENTAL INTERFACIAL TENSION
FOR PROPANE

Temp. °F	d_c (cm)	$\frac{d_e^2}{H}$	ρ_l (gm./cm.^{3})	ρ_v (gm./cm.^{3})	γ Dynes/cm.
120.6	0.1067	0.00977	0.4580	0.0381	4.02
120.6	0.1067	0.01002	0.4580	0.0381	4.12
120.6	0.1067	0.00985	0.4580	0.0381	4.05
120.6	0.1067	0.00974	0.4580	0.0381	4.01
120.6	0.1067	0.00986	0.4580	0.0381	4.06
120.6	0.1067	0.00980	0.4580	0.0381	4.03
158.8	0.1067	0.00600	0.4100	0.0640	2.04
158.8	0.1067	0.00606	0.4100	0.0640	2.05
158.8	0.1067	0.00589	0.4100	0.0640	2.00
158.8	0.1067	0.00597	0.4100	0.0640	2.02
158.8	0.1067	0.00606	0.4100	0.0640	2.05
158.8	0.1067	0.00615	0.4100	0.0640	2.08
158.8	0.1067	0.00617	0.4100	0.0640	2.09
178.7	0.09144	0.00342	0.3570	0.0890	0.90
178.7	0.09144	0.00348	0.3570	0.0890	0.91
178.7	0.09144	0.00344	0.3570	0.0890	0.90
178.7	0.09144	0.00351	0.3570	0.0890	0.92
178.7	0.09144	0.00346	0.3570	0.0890	0.91
178.7	0.09144	0.00342	0.3570	0.0890	0.90
189.8	0.05588	0.00225	0.3410	0.1067	0.52
189.8	0.05588	0.00229	0.3410	0.1067	0.52
189.8	0.05588	0.00221	0.3410	0.1067	0.51
189.8	0.05588	0.00228	0.3410	0.1067	0.52
189.8	0.05588	0.00222	0.3410	0.1067	0.51

TABLE XI

EXPERIMENTAL INTERFACIAL TENSION FOR
26% ETHANE
74% PROPANE

Temp. °F	d_c (cm)	$\frac{d_e^2}{H}$	ρ_l (gm./cm.^{3})	ρ_v (gm./cm.^{3})	γ Dynes/cm.
120.2	0.09144	0.00728	0.4141	0.0532	2.52
120.2	0.09144	0.00711	0.4141	0.0532	2.54
120.0	0.09144	0.00717	0.4141	0.0532	2.58
120.2	0.09144	0.00729	0.4141	0.0532	2.58
120.2	0.09144	0.00728	0.4141	0.0532	2.58
120.2	0.09144	0.00757	0.4141	0.0532	2.68
140.4	0.09144	0.00535	0.3847	0.0718	1.64
140.4	0.09144	0.00510	0.3847	0.0718	1.56
140.4	0.09144	0.00515	0.3847	0.0718	1.58
140.4	0.09144	0.00501	0.3847	0.0718	1.54
140.4	0.09144	0.00536	0.3847	0.0718	1.64
140.4	0.09144	0.00515	0.3847	0.0718	1.58
140.4	0.09144	0.00530	0.3847	0.0718	1.63
140.4	0.09144	0.00534	0.3847	0.0718	1.64
140.4	0.09144	0.00531	0.3847	0.0718	1.63
145.1	0.05588	0.00614	0.3767	0.0774	1.80
145.1	0.05588	0.00549	0.3767	0.0774	1.61
145.1	0.05588	0.00529	0.3767	0.0774	1.55
145.1	0.05588	0.00605	0.3767	0.0774	1.78
149.6	0.05588	0.00516	0.3684	0.0833	1.44
149.6	0.05588	0.00483	0.3684	0.0833	1.35
149.6	0.05588	0.00419	0.3684	0.0833	1.17
149.6	0.05588	0.00563	0.3684	0.0833	1.57

TABLE XII

EXPERIMENTAL INTERFACIAL TENSION FOR
66% ETHANE
34% PROPANE

Temp. °F	d_c (cm)	$\frac{d_e^2}{H}$	ρ_l (gm./cm.^{3})	ρ_v (gm./cm.^{3})	γ Dynes/cm.
99.8	0.05588	0.00405	0.3681	0.0743	1.17
99.8	0.05588	0.00401	0.3681	0.0743	1.15
99.8	0.05588	0.00435	0.3681	0.0743	1.25
99.8	0.05588	0.00442	0.3681	0.0743	1.27
99.8	0.05588	0.00520	0.3681	0.0743	1.50
99.8	0.05588	0.00519	0.3681	0.0743	1.49
109.6	0.05588	0.00286	0.3490	0.0878	0.73
109.6	0.05588	0.00282	0.3490	0.0878	0.72
109.6	0.05588	0.00298	0.3490	0.0878	0.76
109.6	0.05588	0.00286	0.3490	0.0878	0.73
109.6	0.05588	0.00307	0.3490	0.0878	0.79
114.7	0.05588	0.00297	0.3372	0.0964	0.70
114.7	0.05588	0.00303	0.3372	0.0964	0.72
114.7	0.05588	0.00254	0.3372	0.0964	0.60
114.7	0.05588	0.00290	0.3372	0.0964	0.68
114.7	0.05588	0.00275	0.3372	0.0964	0.65
120.0	0.05588	0.00236	0.3228	0.1072	0.50
120.0	0.05588	0.00216	0.3228	0.1072	0.46
120.0	0.05588	0.00224	0.3228	0.1072	0.47
120.0	0.05588	0.00210	0.3228	0.1072	0.44
120.0	0.05588	0.00213	0.3228	0.1072	0.45
120.0	0.05588	0.00211	0.3228	0.1072	0.44
122.1	0.05588	0.00153	0.3163	0.1118	0.31
122.1	0.05588	0.00144	0.3163	0.1118	0.29
122.1	0.05588	0.00133	0.3163	0.1118	0.27
122.1	0.05588	0.00147	0.3163	0.1118	0.30
122.1	0.05588	0.00143	0.3163	0.1118	0.29

TABLE XIII

EXPERIMENTAL INTERFACIAL TENSION
FOR NORMAL BUTANE

Temp. °F	d_c (cm)	$\frac{d_e^2}{H}$	ρ_l (gm./cm.^{3})	ρ_v (gm./cm.^{3})	γ Dynes/cm.
125.6	0.14740	0.01799	0.5338	0.0128	9.19
125.6	0.14740	0.01759	0.5338	0.0128	8.98
125.6	0.14740	0.01774	0.5338	0.0128	9.06
125.6	0.14740	0.01769	0.5338	0.0128	9.03
125.6	0.14740	0.01750	0.5338	0.0128	8.93
125.6	0.14740	0.01762	0.5338	0.0128	9.00
150.3	0.14740	0.01502	0.5198	0.0178	7.39
150.3	0.14740	0.01556	0.5198	0.0178	7.66
150.3	0.14740	0.01534	0.5198	0.0178	7.55
150.3	0.14740	0.01577	0.5198	0.0178	7.76
150.3	0.14740	0.01538	0.5198	0.0178	7.56
150.3	0.14740	0.01540	0.5198	0.0178	7.58
150.3	0.14740	0.01583	0.5198	0.0178	7.79
200.6	0.09144	0.01142	0.4725	0.0333	4.91
200.6	0.09144	0.01075	0.4725	0.0333	4.62
200.6	0.09144	0.01084	0.4725	0.0333	4.66
200.6	0.09144	0.01126	0.4725	0.0333	4.85
200.6	0.09144	0.01125	0.4725	0.0333	4.84
200.6	0.09144	0.01068	0.4725	0.0333	4.60
224.6	0.09144	0.00879	0.4469	0.0450	3.46
224.6	0.09144	0.00866	0.4469	0.0450	3.41
224.6	0.09144	0.00858	0.4469	0.0450	3.38
224.6	0.09144	0.00867	0.4469	0.0450	3.42
224.6	0.09144	0.00912	0.4469	0.0450	3.59
249.4	0.09144	0.00595	0.4156	0.0621	2.06
249.4	0.09144	0.00598	0.4156	0.0621	2.07
249.4	0.09144	0.00602	0.4156	0.0621	2.09
249.4	0.09144	0.00585	0.4156	0.0621	2.03
249.4	0.09144	0.00578	0.4156	0.0621	2.00
275.8	0.05588	0.00302	0.3748	0.0865	0.85
275.8	0.05588	0.00320	0.3748	0.0865	0.90
275.8	0.05588	0.00305	0.3748	0.0865	0.86
275.8	0.05588	0.00290	0.3748	0.0865	0.82
285.0	0.05588	0.00235	0.3556	0.1020	0.58
285.0	0.05588	0.00222	0.3556	0.1020	0.55
285.0	0.05588	0.00216	0.3556	0.1020	0.54
285.0	0.05588	0.00214	0.3556	0.1020	0.53
285.0	0.05588	0.00219	0.3556	0.1020	0.54
285.0	0.05588	0.00226	0.3556	0.1020	0.56
285.0	0.05588	0.00230	0.3556	0.1020	0.57

TABLE XIV

EXPERIMENTAL INTERFACIAL TENSION FOR
30% PROPANE
70% NORMAL BUTANE

Temp. °F	d_c (cm)	$\frac{d_e^2}{H}$	ρ_l (gm./cm.^{3})	ρ_v (gm./cm.^{3})	γ Dynes/cm.
124.3	0.09144	0.01738	0.5162	0.0176	8.49
124.3	0.09144	0.01743	0.5162	0.0176	8.52
124.3	0.09144	0.01753	0.5162	0.0176	8.57
124.3	0.09144	0.01723	0.5162	0.0176	8.42
124.3	0.09144	0.01714	0.5162	0.0176	8.38
124.3	0.09144	0.01792	0.5162	0.0176	8.76
124.3	0.09144	0.01768	0.5162	0.0176	8.64
150.2	0.09144	0.01456	0.4948	0.0247	6.71
150.2	0.09144	0.01450	0.4948	0.0247	6.68
150.2	0.09144	0.01475	0.4948	0.0247	6.80
150.2	0.09144	0.01479	0.4948	0.0247	6.81
150.2	0.09144	0.01476	0.4948	0.0247	6.80
199.1	0.09144	0.00968	0.4474	0.0453	3.82
199.1	0.09144	0.00926	0.4474	0.0453	3.65
199.1	0.09144	0.00916	0.4474	0.0453	3.61
199.1	0.09144	0.00957	0.4474	0.0453	3.77
199.1	0.09144	0.00938	0.4474	0.0453	3.70
224.2	0.09144	0.00620	0.4168	0.0628	2.15
224.2	0.09144	0.00654	0.4168	0.0628	2.27
224.2	0.09144	0.00627	0.4168	0.0628	2.17
224.2	0.09144	0.00630	0.4168	0.0628	2.18
224.2	0.09144	0.00635	0.4168	0.0628	2.20
224.2	0.09144	0.00659	0.4168	0.0628	2.29
224.2	0.09144	0.00668	0.4168	0.0628	2.32
248.4	0.05588	0.00241	0.3786	0.0887	0.68
248.4	0.05588	0.00248	0.3786	0.0887	0.70
248.4	0.05588	0.00258	0.3786	0.0887	0.73
248.4	0.05588	0.00255	0.3786	0.0887	0.72
248.4	0.05588	0.00241	0.3786	0.0887	0.68
248.4	0.05588	0.00259	0.3786	0.0887	0.74
260.8	0.05588	0.00108	0.3516	0.1099	0.26
260.8	0.05588	0.00106	0.3516	0.1099	0.25
260.8	0.05588	0.00101	0.3516	0.1099	0.24
260.8	0.05588	0.00103	0.3516	0.1099	0.24

TABLE XV

EXPERIMENTAL INTERFACIAL TENSION FOR
73% PROPANE
27% NORMAL BUTANE

Temp. °F.	d_c (cm)	$\frac{d_e^2}{H}$	ρ_l (gm./cm.^{3})	ρ_v (gm./cm.^{3})	γ Dynes/cm.
150.4	0.05588	0.01104	0.4514	0.0396	4.46
150.4	0.05588	0.01100	0.4514	0.0396	4.44
150.4	0.05588	0.01115	0.4514	0.0396	4.50
150.4	0.05588	0.01055	0.4514	0.0396	4.26
150.4	0.05588	0.01093	0.4514	0.0396	4.41
150.4	0.05588	0.01113	0.4514	0.0396	4.49
150.4	0.05588	0.01077	0.4514	0.0396	4.34
175.5	0.05588	0.00735	0.4219	0.0554	2.64
175.5	0.05588	0.00725	0.4219	0.0554	2.60
175.5	0.05588	0.00731	0.4219	0.0554	2.62
175.5	0.05588	0.00738	0.4219	0.0554	2.65
175.5	0.05588	0.00702	0.4219	0.0554	2.52
175.5	0.05588	0.00668	0.4219	0.0554	2.40
175.5	0.05588	0.00686	0.4219	0.0554	2.46
196.7	0.05588	0.00557	0.3913	0.0748	1.73
196.7	0.05588	0.00597	0.3913	0.0748	1.85
209.1	0.05588	0.00375	0.3687	0.0908	1.02
209.1	0.05588	0.00364	0.3687	0.0908	0.99
209.1	0.05588	0.00372	0.3687	0.0908	1.01
209.1	0.05588	0.00380	0.3687	0.0908	1.03
209.1	0.05588	0.00374	0.3687	0.0908	1.02
224.8	0.05588	0.00176	0.3280	0.1233	0.35
224.8	0.05588	0.00180	0.3280	0.1233	0.36
224.8	0.05588	0.00168	0.3280	0.1233	0.34
224.8	0.05588	0.00169	0.3280	0.1233	0.34
224.8	0.05588	0.00180	0.3280	0.1233	0.36
224.8	0.05588	0.00156	0.3280	0.1233	0.31
229.6	0.05588	0.00088	0.3080	0.1414	0.14
229.6	0.05588	0.00100	0.3080	0.1414	0.16

TABLE XVI

EXPERIMENTAL INTERFACIAL TENSION FOR ISOBUTANE

Temp. °F	d_c (cm)	$\frac{d_e^2}{H}$	ρ_l (gm./cm.^{3})	ρ_v (gm./cm.^{3})	γ Dynes/cm.
125.2	0.09144	0.01459	0.4930	0.0170	6.81
125.2	0.09144	0.01431	0.4930	0.0170	6.68
125.2	0.09144	0.01424	0.4930	0.0170	6.64
125.2	0.09144	0.01458	0.4930	0.0170	6.80
125.2	0.09144	0.01450	0.4930	0.0170	6.76
125.2	0.09144	0.01451	0.4930	0.0170	6.77
150.1	0.09144	0.01304	0.4735	0.0235	5.75
150.1	0.09144	0.01285	0.4735	0.0235	5.66
150.1	0.09144	0.01256	0.4735	0.0235	5.54
150.1	0.09144	0.01283	0.4735	0.0235	5.66
150.1	0.09144	0.01309	0.4735	0.0235	5.77
150.1	0.09144	0.01294	0.4735	0.0235	5.71
175.1	0.09144	0.01036	0.4517	0.0325	4.26
175.1	0.09144	0.01047	0.4517	0.0325	4.30
175.1	0.09144	0.01055	0.4517	0.0325	4.33
175.1	0.09144	0.01026	0.4517	0.0325	4.22
200.2	0.09144	0.00824	0.4267	0.0452	3.08
200.2	0.09144	0.00798	0.4267	0.0452	2.98
200.2	0.09144	0.00780	0.4267	0.0452	2.91
200.2	0.09144	0.00770	0.4267	0.0452	2.88
200.2	0.09144	0.00763	0.4267	0.0452	2.85
200.2	0.09144	0.00806	0.4267	0.0452	3.01
224.9	0.05588	0.00500	0.3974	0.0629	1.64
224.9	0.05588	0.00499	0.3974	0.0629	1.63
224.9	0.05588	0.00510	0.3974	0.0629	1.67
224.9	0.05588	0.00496	0.3974	0.0629	1.62
224.9	0.05588	0.00504	0.3974	0.0629	1.65
247.5	0.05588	0.00277	0.3623	0.0890	0.74
247.5	0.05588	0.00272	0.3623	0.0890	0.73
247.5	0.05588	0.00259	0.3623	0.0890	0.69
247.5	0.05588	0.00274	0.3623	0.0890	0.73
262.6	0.05588	0.00125	0.3275	0.1214	0.25
262.6	0.05588	0.00122	0.3275	0.1214	0.25
262.6	0.05588	0.00125	0.3275	0.1214	0.25
262.6	0.05588	0.00118	0.3275	0.1214	0.24
262.6	0.05588	0.00121	0.3275	0.1214	0.24
262.6	0.05588	0.00125	0.3275	0.1214	0.25
262.6	0.05588	0.00129	0.3275	0.1214	0.26
262.6	0.05588	0.00115	0.3275	0.1214	0.23
262.6	0.05588	0.00132	0.3275	0.1214	0.27

TABLE XVII

EXPERIMENTAL INTERFACIAL TENSION FOR
29% PROPANE
71% ISOBUTANE

Temp. °F	d_c (cm)	$\frac{d_e^2}{H}$	ρ_l (gm./cm.^{3})	ρ_v (gm./cm.^{3})	γ Dynes/cm.
124.2	0.05588	0.01325	0.4832	0.0216	5.99
124.2	0.05588	0.01319	0.4832	0.0216	5.97
124.2	0.05588	0.01424	0.4832	0.0216	6.44
124.2	0.05588	0.01362	0.4832	0.0216	6.16
149.8	0.05588	0.01161	0.4611	0.0301	4.90
149.8	0.05588	0.01153	0.4611	0.0301	4.87
149.8	0.05588	0.01159	0.4611	0.0301	4.90
149.8	0.05588	0.01205	0.4611	0.0301	5.09
173.3	0.05588	0.00899	0.4384	0.0410	3.50
173.3	0.05588	0.00929	0.4384	0.0410	3.62
173.3	0.05588	0.00915	0.4384	0.0410	3.56
173.3	0.05588	0.00904	0.4384	0.0410	3.52
199.8	0.05588	0.00630	0.4080	0.0585	2.16
199.8	0.05588	0.00640	0.4080	0.0585	2.19
199.8	0.05588	0.00640	0.4080	0.0585	2.19
199.8	0.05588	0.00594	0.4080	0.0585	2.03
199.8	0.05588	0.00606	0.4080	0.0585	2.07
199.8	0.05588	0.00604	0.4080	0.0585	2.07
199.8	0.05588	0.00630	0.4080	0.0585	2.16
199.8	0.05588	0.00626	0.4080	0.0585	2.14
199.8	0.05588	0.00635	0.4080	0.0585	2.17
223.7	0.05588	0.00359	0.3729	0.0836	1.02
223.7	0.05588	0.00344	0.3729	0.0836	0.98
223.7	0.05588	0.00337	0.3729	0.0836	0.96
223.7	0.05588	0.00335	0.3729	0.0836	0.95
223.7	0.05588	0.00331	0.3729	0.0836	0.94
223.7	0.05588	0.00356	0.3729	0.0836	1.01
223.7	0.05588	0.00353	0.3729	0.0836	1.00
223.7	0.05588	0.00334	0.3729	0.0836	0.95
236.6	0.05588	0.00205	0.3472	0.1057	0.48
236.6	0.05588	0.00208	0.3472	0.1057	0.49
236.6	0.05588	0.00210	0.3472	0.1057	0.50
236.6	0.05588	0.00196	0.3472	0.1057	0.46
236.6	0.05588	0.00214	0.3472	0.1057	0.51
236.6	0.05588	0.00200	0.3472	0.1057	0.47
236.6	0.05588	0.00208	0.3472	0.1057	0.49

TABLE XVII (Continued)

Temp. °F	d_c (cm)	$\frac{d_e^2}{H}$	ρ_l (gm./cm.^{3})	ρ_v (gm./cm.^{3})	γ Dynes/cm.
244.6	0.05588	0.00136	0.3258	0.1302	0.26
244.6	0.05588	0.00133	0.3258	0.1302	0.25
244.6	0.05588	0.00140	0.3258	0.1302	0.27
244.6	0.05588	0.00125	0.3258	0.1302	0.24
244.6	0.05588	0.00134	0.3258	0.1302	0.26
244.6	0.05588	0.00138	0.3258	0.1302	0.26
244.6	0.05588	0.00136	0.3258	0.1302	0.26
244.6	0.05588	0.00131	0.3258	0.1302	0.25
244.6	0.05588	0.00139	0.3258	0.1302	0.27
244.6	0.05588	0.00128	0.3258	0.1302	0.25

TABLE XVIII

EXPERIMENTAL INTERFACIAL TENSION FOR
70% PROPANE
30% ISOBUTANE

Temp. °F	d_c (cm)	$\frac{d_e^2}{H}$	ρ_l (gm./cm.^{3})	ρ_v (gm./cm.^{3})	γ Dynes/cm.
126.1	0.05588	0.01162	0.4626	0.0304	4.92
126.1	0.05588	0.01171	0.4626	0.0304	4.96
126.1	0.05588	0.01168	0.4626	0.0304	4.95
126.1	0.05588	0.01231	0.4626	0.0304	5.21
126.1	0.05588	0.01114	0.4626	0.0304	4.72
126.1	0.05588	0.01181	0.4626	0.0304	5.00
126.1	0.05588	0.01128	0.4626	0.0304	4.78
150.5	0.05588	0.00876	0.4374	0.0421	3.39
150.5	0.05588	0.00884	0.4374	0.0421	3.42
150.5	0.05588	0.00888	0.4374	0.0421	3.44
150.5	0.05588	0.00876	0.4374	0.0421	3.39
150.5	0.05588	0.00921	0.4374	0.0421	3.56
176.0	0.05588	0.00647	0.4062	0.0601	2.20
176.0	0.05588	0.00648	0.4062	0.0601	2.20
176.0	0.05588	0.00671	0.4062	0.0601	2.28
176.0	0.05588	0.00663	0.4062	0.0601	2.25
176.0	0.05588	0.00645	0.4062	0.0601	2.19
176.0	0.05588	0.00647	0.4062	0.0601	2.20
176.0	0.05588	0.00648	0.4062	0.0601	2.20
176.0	0.05588	0.00638	0.4062	0.0601	2.16
200.6	0.05588	0.00369	0.3666	0.0884	1.00
200.6	0.05588	0.00337	0.3666	0.0884	0.92
200.6	0.05588	0.00361	0.3666	0.0884	0.98
200.6	0.05588	0.00345	0.3666	0.0884	0.94
200.6	0.05588	0.00348	0.3666	0.0884	0.95
200.6	0.05588	0.00358	0.3666	0.0884	0.98
200.6	0.05588	0.00339	0.3666	0.0884	0.92
200.6	0.05588	0.00353	0.3666	0.0884	0.96
215.1	0.05588	0.00164	0.3319	0.1206	0.34
215.1	0.05588	0.00169	0.3319	0.1206	0.35
215.1	0.05588	0.00164	0.3319	0.1206	0.34
215.1	0.05588	0.00164	0.3319	0.1206	0.34
215.1	0.05588	0.00168	0.3319	0.1206	0.35
219.1	0.05588	0.00115	0.3182	0.1397	0.20
219.1	0.05588	0.00115	0.3182	0.1397	0.20
219.1	0.05588	0.00120	0.3182	0.1397	0.21
219.9	0.05588	0.00100	0.3147	0.1421	0.17
219.9	0.05588	0.00100	0.3147	0.1421	0.17
219.9	0.05588	0.00098	0.3147	0.1421	0.17
219.9	0.05588	0.00101	0.3147	0.1421	0.17
219.9	0.05588	0.00096	0.3147	0.1421	0.16

APPENDIX C

ESTIMATE OF ERRORS

Estimate of Errors

Expressions for the most probable value of error in interfacial tension as a result of experimentally determined quantities were developed by Deam (3). Since the method of measuring the drop diameters and the correlations used to determine the density difference in this work were similar to those of Deam, these expressions were adopted for use in this work. The expressions for errors in interfacial tension resulting from errors in the gravitational constant, the density difference, the equatorial diameter, and the selected plane diameter were given as shown in Equations (8), (9), (10), and (11), respectively.

Gravitational constant:

$$\gamma_g = \left(\frac{\partial\gamma}{\partial g}\right)\delta_g = \left(\Delta\rho\left(\frac{1}{H}\right){d_e}^2\right)\delta_g = \left(\frac{\gamma}{g}\right)\delta_g \tag{8}$$

Density difference:

$$\gamma_{\Delta\rho} = \left(\frac{\partial\gamma}{\partial\Delta\rho}\right)\delta_{\Delta\rho} = \left(g\left(\frac{1}{H}\right){d_e}^2\right)\delta_{\Delta\rho} \tag{9}$$

Equatorial diameter:

$$\gamma_{d_e} = \left(\frac{\partial\gamma}{\partial d_e}\right)\delta_{d_e} = 4.6444\left(\frac{\gamma}{d_e}\right)\delta_{d_e} \tag{10}$$

Selected plane diameter:

$$\gamma_{d_s} = \left(\frac{\partial\gamma}{\partial d_s}\right)\delta_{d_s} = -2.6444\left(\frac{\gamma}{d_s}\right)\delta_{d_s} \tag{11}$$

The most probable error in interfacial tension given as a function of these errors is shown in Equation (12).

$$\Delta\gamma = \left(\gamma_g^{\ 2} + \gamma_{\Delta\rho}^{\ 2} + \gamma_{d_e}^{\ 2} + \gamma_{d_s}^{\ 2} \right)^{1/2} \tag{12}$$

Typical values of the experimentally measured quantities were used to compute the most probable error in interfacial tension from this equation. The errors in these quantities were the smallest errors that reasonably could be expected. The values for a set of data from the seventy per cent propane in isobutane binary are

$$d_e = 0.1170 \text{ cm.}$$

$$d_s = 0.0889 \text{ cm.}$$

$$\Delta\rho = 0.3953 \text{ gm./c.c.}$$

$$g = 980 \text{ cm./sec.}^2$$

$$\gamma = 3.44 \text{ dynes/cm.}$$

The following uncertaities were assumed:

$$\delta \ = 0 \text{ cm./sec.}^2$$

$$\delta_{\Delta\rho} = 0.01 \text{ gm./c.c.}$$

$$\delta_{d_e} = 0.001 \text{ cm.}$$

$$\delta_{d_s} = 0.001 \text{ cm.}$$

The most probable value of error in interfacial tension computed from Equation (12) is

$$\Delta\gamma = 0.19 \text{ dynes/cm.}$$

For the data point considered,

$$\gamma = 3.44 \pm 0.19 \text{ dynes/cm.}$$

VITA

Larry Dean Swales

Candidate for the Degree of

Master of Science

Thesis: INTERFACIAL TENSION IN LIGHT HYDROCARBON BINARY SYSTEMS

Major Field: Chemical Engineering

Biographical:

Personal Data: Born in Clearfield, Pennsylvania, August 24, 1949, the son of Mr. and Mrs. Ernest Paul Swales; Married to Rosalyn Rita Nicholas, May 15, 1971.

Education: Graduated from Eisenhower High School in Lawton, Oklahoma, in May, 1967; received degree of Bachelor of Science in Chemical Engineering from Oklahoma State University in May, 1971; completed requirements for degree of Master of Science at Oklahoma State University in July, 1972.

Membership in Scholarly or Professional Societies: Sigma Tau, Omega Chi Epsilon, Phi Kappa Phi, Omicron Delta Kappa, Affiliate Member of the American Institute of Chemical Engineers.

Professional Experience: Graduate teaching assistant, School of Chemical Engineering, Oklahoma State University, 1971-1972; employed by Humble Oil and Refining Company, Baton Rouge, Louisiana, as a process engineer during the summer of 1971.